ESTIMATING MEASUREMENT UNCERTAINTY FOR PARTICULATE EMISSIONS FROM STATIONARY SOURCES

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ABSTRACT

Quantifying or estimating emission uncertainty for particulate matter from stationary sources in South Africa.

The estimation of measurement uncertainty with regards to hazardous air pollution emissions from stationary sources is currently the most uncertain element associated with obtaining relevant, valid stack emission data in South Africa. This project is aimed at developing an appropriate method to evaluate the uncertainty associated with particulate matter measurements conducted for stationary source emissions in the South African context. A series of In-Stack measurements were taken in accordance with recognized international methodology (ISO 9096:1992, and 2003) on two different industrial processes, representing a best and worst case scenario. A comparison between the two scenarios was made in an attempt to establish what components of the sampling technique have the greatest error.

The effect of cumulative errors in the sampling train as well as external factors that may influence the results were evaluated and included in the final estimate of uncertainty. Some of the factors used included the sampling location, industrial process and external environmental factors.

The overarching goal of this project was to establish an estimate of the cumulative uncertainty on the final emission values obtained, inclusive of both analytical, field sampling and process related variables that may result in a cumulative error associated with quantifying stationary source particulate matter emission values.

The results of the study found that the estimated combined expanded uncertainty for both sets of data was calculated to be between 62 – 72%. Upon closer analysis of the data it was ascertained that the data obtained were inadequate and the calculation of the uncertainty of the results both with the compliant and non-compliant sampling campaigns revealed that the variability of the results was too great for both scenarios to make any statistically valid observations or conclusions about the data.

In lieu of this, and considering the significant costs, time and labour involved in order to obtain enough data to enable adequate quantification of an uncertainty budget for the results obtained, the author has developed an alternative tool for assessing the quality and reliability of reported emission figures. The author has developed what he has named a sampling suitability matrix, this tool although subjective in nature will add significant value (in the authors opinion) to the interpretation of the quality and reliability of the final emission results reported. The intention of this tool is to be incorporated as supplementary information into all emission reports in future. This will enable the plant operator and regulator to assess the quality of reported data and final emission results, thus assisting in establishing whether the plant is in compliance with their Air Emission License (AEL) requirements or not.

I declare this research report is my own, unaided work
in fulfillment of the requirements of the degree
of Master of Science in Geography and Environmental Science,
in the University of the Witwatersrand, Johannesburg.
It has not been submitted previously for any degree
Or examination in any other university

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PREFACE

The need for the validation of stack emission data in South Africa is absolutely critical in ensuring that the correct decisions are made regarding issues around air pollution problems and broad-based sustainable development. Obtaining accurate, reliable and valid yet cost effective data is critical in ensuring that this can be implemented. As a means to an end, the inclusion of the estimation of the uncertainty of a final measurement result in an emissions report will prove to be invaluable in the decision and policy making process.

Uncertainty arises due to a lack of knowledge regarding the true value of a quantity (Frey, 1998). Old measurement standards do not mention uncertainty; in older particulate matter standards the term “accuracy” is used but measurement uncertainty is probably implied without specifying the confidence limit (Lewandowski et al., 2004).

The term uncertainty usually describes the range of values that the true value can be expected to fall within at the user specified level of probability (Lewandowski et al., 2004). It is for this reason that most methods require revisiting the issue of uncertainty and may require conducting additional validation tests to be able to form a view on their uncertainty at a limit value (Lewandowski et al., 2004).

The high costs associated with conducting sampling campaigns to obtain reliable data are a major stumbling block in a developing country such as South Africa. In the authors opinion gained from years of experience in the industry, many plant operators have made and continue to make great strides in ensuring compliance with relevant environmental regulations. However, the tendency of industry is to save costs in the short term by undertaking measurement campaigns where the minimum requirements set out in the relevant sampling standards are not met or utilise unapproved or unvalidated sampling techniques or analytical methods.. This approach may save a few thousand Rands on analysis in the short term; however it may cost millions of Rands in the long term as a result of misrepresentative or unreliable data. A costly error due to decisions taken on questionable data is a situation that a country such as

South Africa can ill afford. This is the main thrust behind the effort to validate the emissions data obtained in South Africa. The correct determination of the measurement uncertainty of results used for regulatory and policy decisions is critical (Robinson, 2004). This can only be achieved by ensuring that quality and reliable stack emission data are obtained in South Africa.

The management of air pollution issues in South Africa is currently in a state of flux. Some guidance is in place for the determination and control of pollutants from source emissions, however, there is much need for clarity and reform as the legislation, although well written, has encountered several obstacles in the practical implementation of the legal requirements. A major issue is that the legislation requires any test house or laboratory conducting stack emission surveys or analysis to be accredited to ISO17025. No test house in South Africa is currently accredited in terms of this requirement and the situation needs to be remedied as soon as possible. The implementation of the new legislation in South Africa (National Environmental Management: Air Quality Act, 2004 [Act 39:2004] and specifically the section 21 regulations) is not without its teething problems. The intent of the new legislation is to reform the control of air pollution, bringing a paradigm shift to air pollution control, moving from source based control to the control of air pollution in the receiving environment.

Air pollution sampling techniques, and adopted international methodologies currently in use in South Africa are in much need of reform. This reformation is necessary in order to provide clear guidance in determining the extent and characterization of the air pollutants from stationary sources emitted by South African industries. It is also necessary in order to standardize the technique used so that a comparison of reported emissions can be performed. The calculation and estimation of the level of uncertainty of measurements and analytical procedures has been identified as a critical component in ascertaining the validity and ultimately the reliability of emissions data obtained in South Africa.

Due to limited resources available and calls from Industry, the need to quantify, calculate and estimate the uncertainty of measurement with regards to stationary source emissions will prove an invaluable tool for industry in establishing permit

compliance. By estimating the uncertainty of measurement data, the magnitude of certain perceived problems can be quantified and factored into the decision making process. The main focus of this project is to develop a standardized methodology for the assessment of data quality, for example if a value of 150 mg/Nm^3 of total particulate matter is reported to be present within an off-gas stream or being emitted from a stationary source, it is important to know the extent to which that value is reliable, and what error or uncertainty can one assign to the value. If one can adequately estimate the uncertainty or the quality of emissions data, then the decision making process and plan of action can be more accurately and cost effectively implemented.

Contents

ABBREVIATIONS AND ACRONYMS

ISO	International Standards Organization
NEMA	National Environmental Management Act
GUM	Guide to the Expression of Uncertainty in Measurement
USEPA	United States Environmental Protection Agency
LV	Limit Value
SD	Standard Deviation
CI	Confidence Interval
NPL	National Physical Laboratory
AQA	Air Quality Act
WID	Waste Incineration Directive
LCPD	Large Combustion Plant Directive
AEL	Air Emission License

CHAPTER 1: INTRODUCTION

1.1 PROJECT OVERVIEW

In 2004 the National Environmental Management Act (NEMA) and regulations were promulgated and by 2010 were gazetted for the first time in South Africa. Under the NEMA, the Air Quality Act of 2004 ("Act 39:2004") (AQA) was promulgated and included priority pollutants identified by the Department of Environmental Affairs (DEA) as having, or may have, a significant detrimental effect on the environment, including health, social conditions, economic conditions, ecological conditions or cultural heritage. In this context, particulate matter was identified as one of the main priority pollutants that may cause harm as the requirement to measure for particulate matter is contained in almost every category for listed activities under section 21 of the National Environmental Management: Air Quality Act,2004(Act no. 39 of 2004).

The uncertainty of these measurements is difficult to quantify due to the physical nature of particles which may affect their behavior in an off-gas stream. To compensate for the maldistribution of particles in the gas stream, the samples are extracted Isokinetically from the gas stream utilising recognized, validated methods such as the USEPA Method 5/17 and ISO9096:1992/2003.

Good quality data are essential in the decision making process for plant operators and regulatory authorities alike. Decisions made on questionable data can lead to costly mistakes from upgrading plant off-gas cleaning systems unnecessarily, to not taking action where necessary as a result of questionable data. The air quality monitoring field is still in its relative infancy in South Africa. The implementation of the new air quality legislation (National Air Quality Act, Act 39:2004) is an ongoing process and is not without its teething problems. This project aims to coincide with the demands of the new legislation in order to ensure data quality and reliability of reported results. The implementation of a standardized methodology to assess data quality is the ultimate goal of this project.

Measurement uncertainty attempts to quantify the unknown inherent in a measurement result. The uncertainty assigned to a result represents the range of values about the results in which the true value is expected to lie (Robinson, 2004). Indeed the most certain aspect in air quality emissions monitoring is that the uncertainty reported with emission results is of utmost importance when drawing conclusions from the data and assessing whether a plant is indeed compliant with the relevant limits as stipulated in the plant's Air Emission License (AEL).

It should be stressed that this true value is a conceptual term, which can never be exactly determined. All measurements have an associated uncertainty; the goal is to quantify this uncertainty so that the results can be properly interpreted. The statement of uncertainty includes a value for the degree of confidence. This quantifies the expectation that the true value lies within the region defined by the uncertainty. It is usual for uncertainty to be required to be calculated with a 95% level of confidence (Robinson, 2004).

Scientific literature on the subject of uncertainty for stack / point source monitoring is very limited and is mainly presented in unpublished articles and is contained in the standard reference methods and technical guidance notes published by the United Kingdom Environmental Agency amongst others (Coleman, 2015).

As a result of the limited published scientific literature available the "Guide to the Expression of Uncertainty of Measurement" (GUM, 1995) is utilized almost exclusively by the measurement community as the overarching document in assessing measurement uncertainties in stack emission monitoring, with more recent publications being mere commentary and guidance documents on how to interpret and apply this guide (Robinson, 2002). For this reason and to ensure a certain level of consistency the GUM has been utilized as the primary guidance document for determining the uncertainty of measurement in this paper.

The main reason that the GUM has been almost exclusively adopted is due to the fact that the guide was developed by a joint working group consisting of experts nominated by the following organizations: Bureau International des Poids et Mesures (BIPM), International Electrotechnical Commission (IEC), the International Organization for Standardization (ISO), and the international organization of legal

metrology (OIML). In addition, the following organizations supported its development: International Federation of clinical Chemistry (IFCC), International Union of Pure and Applied Chemistry (IUPAC) and International Union of Pure and Applied Physics (IUPAP).

One of the main shortfalls in South Africa is that there is currently no accreditation or certification body for source monitoring organizations in the country. As a result, standardisation of test methods and inter-laboratory comparisons and studies have little or no value, as validation of the methods cannot be carried out without a conflict of interest or the necessary certifications of the measurement bodies involved. Hence, there is no way to ensure standard procedures are followed strictly so that the values can be compared once obtained. This scenario is a major stumbling block in moving the industry forward towards environmental compliance in South Africa. In the interim, this study attempts to fill this gap as a temporary, cost effective solution to determine the extent to which the data in South Africa are representative.

As mentioned previously in the preface, the trend by many industries at present is to save costs by doing the absolute minimum to comply with the relevant standards in an effort to save money. However this may be demonstrated in this study to be short sighted, and may end up being costly in the long term, with non-compliant permit conditions prevailing as a result of poor data quality.

1.2 MAIN OBJECTIVES OF THE STUDY

The main goal and objective of the project is to establish the validity of source emission data (particulate matter emissions) obtained in South Africa. This will be achieved by employing the general approach or framework to calculate uncertainty as set out in the "Guide to the Expression of Uncertainty in Measurement" (GUM, 1995), in which individual uncertainty sources are identified, quantified and combined to provide the measurement uncertainty. This philosophy has been adopted as the underpinning approach within the European and International Standardization bodies and will be used in standardized measurement methods in the future (Robinson, 2004).

For the purposes of this study the ISO 9096:1992 and 2003 methods will be utilized for the measurement campaigns. These methods have been chosen due to the fact that the ISO9096 method was utilized by Levego for the sampling to produce the data sets that will subsequently be utilized in this study. The abovementioned methods are deemed as equivalent methods by the international measurement community and utilizing either method should produce a similar result. The scientific principles of measurement are effectively the same for all the above mentioned standards with minor differences in approach and application between them.

An estimate of the uncertainty of the final emission results and the effects of not adhering to the requirements of the ISO9096 methods will try to be established.

1.3 FINDINGS AND RESEARCH HYPOTHESIS

In reviewing stack emission monitoring surveys conducted in the past, it has been suggested that the greatest components of error are those that are out of control of the sampling specialist. The "International Organization for Standardization ISO 9096, (1992)" method was utilized for conducting the particulate matter measurements for the study, which includes stationary source emissions – the determination of concentration and mass flow rate of particulate material in gas-carrying ducts – and the manual gravimetric method. According to the method, the following parameters are deemed to be out of the control of the sampling specialist: plant operating conditions, environmental conditions, and the non-compliance of the sampling location to the minimum requirements as set out in ISO 9096:1992 and 2003.

If all the minimum components of the standard are complied with then the final reported emission results would be guaranteed to be within $\pm$ 10 % of the reported value (ISO 9096:1992 and 2003). The problem arises when the minimum requirements are not adhered to. In South Africa, most existing industrial plants have been in operation for decades and as a result have been built without due consideration for complying with the minimum current environmental standards. This poses a problem, especially with regards to obtaining a suitably compliant sampling location.

In contrast to the measurement of gaseous emissions which can be routinely undertaken with an accuracy of a few percent, the measurement of particulate emissions is far more difficult. This arises primarily from the maldistribution of particle concentration within the duct or chimney coupled with the non-uniformity of the gas velocity (Hawksley et al., 1977). This may be due to several factors such as bends, dampers etc. in the off-gas ducting. The basic requirement of all extractive sampling techniques is that a sample of the gas taken into the measurement system should be representative of the bulk of the gas stream in the flue. For these reasons, very precise guidelines for particle sampling are required and these are given in the various standard methods (ISO9096:1992/2003 and USEPA 5/17). One can conclude then from the abovementioned properties of particles that firstly the choice of sampling position is vital, and secondly that multipoint sampling should be utilized in almost all applications (Hawksley et al., 1977). The extent of deviations of both the gas velocity and the particle emissions rate which may be experienced in practice are significant and construction costs are a major issue. As the primary objective is to build an industrial plant at the most reasonable cost, enclosed flue off-gas systems are typically designed to be as small and compact as possible. This then makes the adherence to the minimum requirements for a sampling location the most commonly non-compliant parameter (Hawksley et al., 1977).

The reason for the above assumption (non-compliance of the sampling location), is that the laboratory analysis of the samples obtained are done under controlled laboratory conditions to ensure minimal external interference with the sample. The sampling equipment utilized can be adequately controlled by the sampling specialist and all the components of the sampling train can be verified and calibrated where necessary. The plant operating conditions, environmental conditions and sampling location at the time of measurement are however not under the direct control of the sampling specialist and it is for this reason that these scenarios are assumed to form the greatest error component associated with the final emissions result.

From the assumptions of the influence of the compliance of the sampling and field conditions and control under laboratory conditions of the analysis mentioned above, several scientific questions can be asked;

- Does the non-compliance of the sampling location and process operating conditions have the greatest influence on the sampling results?

- Can the uncertainty of the measured emissions be determined statistically?

- Can a suitable method of evaluating the acceptability or quality of final emissions data be developed?

In an attempt to answer these questions, two sampling campaigns have been conducted. The first sampling campaign was conducted where all the minimum requirements of the standard are met. The second sampling campaign was conducted where the minimum requirements for the sampling location and process operations do not adhere to the minimum requirements of the standard. The subsequent comparison and analyses of the data sets obtained from a fully compliant (Source A) and non-compliant (Source B) stack emission campaign will endeavor to answer the abovementioned questions. Once these findings have been established, an endeavor has been undertaken to find ways through statistical treatment of the data to estimate the uncertainty of the measurement when faced with a non-compliant stack.

Whether the estimation of the overall uncertainty is feasible or not, will be determined once the data are evaluated. If it is found that it is not feasible to get any decent estimate of the uncertainty pertaining to the non-compliant measurement scenario, then this study will provide the impetus to inform industry of the potential dire consequences of not spending money on projects to ensure that the sampling locations and plant operations are satisfactory for obtaining good quality emissions data.

The trend by many industries at present is to save costs by doing the bare minimum to comply with the relevant standards in an effort to save money. As South Africa, which is classified as a developing nation, tends to follow developed country trends, it is safe to say that industry will have to start taking environmental issues seriously and spend money to ensure good quality data. Best practice in developed nations is easier to obtain as they tend to have well established standards and norms, whilst in South

Africa one has to generally look abroad for guidance. This situation, although cost effective, is not always appropriate as the standard methods and norms adopted in a developed country may not be entirely relevant or suitable for application in a developing country such as South Africa.

1.3.1 FINDINGS OF ISO 9096: 2003 DUTCH STUDY

According to the findings of the study, the results were disappointing as the reproducibility of the Dutch field study were deemed to be less than satisfactory. During subsequent meetings with the project support committee and members of the quality committee it was established that the performance characteristics of the Netherlands Standardization Institute (NEN)-ISO9096:1992 be related to the characteristic properties of the waste gases. This conclusion is based mainly on the discrepancies in the results of repeatability as determined at the three sources. Two of the three sources show a repeatability of approximately 12-14%, while the third source has a significantly higher repeatability value (and eventually also a disappointing reproducibility). A great difference between the first two and the third source was attributed to the high water vapour content. Moreover, there may be differences in physical composition of the dust in the waste gases. The conclusion, based on the matrix discrepancies in the waste gases, is that evidently a distinction is to be made between ‘simple’ and ‘difficult’ sources. It would appear that ‘difficult’ sources place too high a demand on the measuring method.

On the project support committee’s recommendation and after approval thereof by the quality committee, NOVEM commissioned the performance of supplementary dust measurements on an emission simulation plant as installed at the Hessische Landesanstalt für Umwelt (HLfU) in Kassel, Germany. The purpose hereof is to demonstrate the reproducibility and correctness of measurements for ‘simple’ sources, whereby the result may also serve as a basis for the problems experienced with ‘difficult’ sources. At this plant not only the reproducibility of the measuring method was determined but also its trueness, as well as that of the participating Dutch measuring institutes. The reproducibility was determined at two concentration levels (approximately 10 and 20 mg/m^3). Based on measurements at this plant, a reproducibility of 4.5mg/m^3 (44%) was determined at the concentration level of 10$mg/m^{3"}$

A similar order of magnitude was determined at the 20 mg/m^3 concentration level. When taking these Dutch findings into consideration in the context of this study, the author has come to the conclusion that the errors and uncertainties with regards to spatial and temporal variations are too great to allow much value to be derived from an in-depth statistical analysis of the results obtained, other than to confirm that there are large uncertainties contained in trying to reproduce results utilising this method on various plants – be they compliant or non-compliant. Therefore, the imperative to utilise a qualitative approach to complement the emission result is vital in determining the quality of the results obtained, and ultimately the decisions made.

CHAPTER 2: DATA AND METHODOLOGY

2.1 OVERVIEW

The source emission data utilized in the study were obtained from two stack sampling campaigns conducted for the determination of concentration and mass flow rate of particulate matter. The surveys were undertaken by a leading South African source monitoring organization (Levego, South Africa, 2005).

The first sampling campaign involved conducting stack samples for particulate matter from a large industrial boiler installation, typical of a coal fired power plant found in South Africa (Source A). These data are representative of the best case scenario where the results represent a stack that complies with all the minimum requirements as set out in ISO 9096:1992 and 2003. The second sampling campaign involved stack sampling from a cement kiln installed on a typical cement manufacturing plant (Source B). These data are representative of the worst case scenario where the results represent a stack that does not adhere to all the minimum requirements as set out in ISO 9096:1992 and 2003. The requirements not adhered to are the requirements specifically related to the sampling location.

2.2 DATA

For the purposes of this study, it is assumed that all the minimum requirements that are set out in ISO 9096:1992, and 2003, that are in direct control of the measurement specialist, such as the sampling equipment and subsequent sample analysis in the laboratory, have been adhered to. For both scenarios, compliant (Source A) and non-compliant (Source B), it is also assumed that the equipment, consumables and analyses all comply with the minimum requirements of ISO 9096:1992 and 2003.

The physical characteristics of particulate matter (size, shape, density etc.) are of such a nature that the particles are affected by gravity. Due to this, the particulate matter is not evenly distributed in the gas stream. Therefore, to reduce the impact of the uneven distribution of particles throughout the gas stream, it is critical to have stable uniform flow to allow for accurate isokinetic sampling of the particulate matter (Hawksley et

al., 1977). The suitability of the sampling location has the single biggest effect on the ability to sample isokinetically due to random effects caused by the process and prevailing environmental conditions (Hawksley et al., 1977). The systemic effects are largely under the control of the sampling technician and can therefore be quantified and accounted for.

2.3 DATA HANDLING

- The inclusion and comparison of the flow profile data sets are therefore the most appropriate way to assess the suitability of the sampling location, as an uneven and unstable flow profile is assumed to have the largest single effect on the uncertainty of the final results that are reported A stable flow profile is defined in ISO9096 as adhering to the following minimum requirements;
- Angle of flow less than 15 degrees to the sampling plane
- Pressure difference (Pitot tube) greater than 5 Pa
- Ratio of maximum gas velocity to minimum gas velocity 3:1
- No negative flow present
- Straight length of duct before sampling point greater than 5 hydraulic diameters
- Straight length of duct after sampling point greater than 2 hydraulic diameters
- Straight length of duct before emission point greater than 5 hydraulic diameters

2.4 QUALITY MANAGEMENT FOR EMISSIONS MONITORING

The purpose of quality control is to reduce uncertainties in measurements to a minimum according to Technical Guidance Note M2, (2004). Monitoring of stack emissions to air, Environment Agency (Version 3). This guide draws a distinction between two types of uncertainty that arise in emissions monitoring. These may be classified as follows:

i. Random Uncertainties – these give rise to a variation about the mean and tend to exhibit a Gaussian or similar statistical distribution. The degree of confidence that may be assigned to the mean of the measurements, therefore increasing as more samples are taken. Typically random uncertainties arise from small variations in procedure and may be controlled by accurate specification of procedures and by training the operators to ensure that these procedures are followed rigorously (Clarke et al., 1998).

ii. Systematic uncertainties – these introduce a bias into the measurements and do not vary about the mean. These can be reduced by ensuring the use of appropriate equipment, insisting on regular calibration and implementing a regular program of maintenance. Systematic uncertainties also arise from differences in sampling practice between operators. These latter uncertainties are the most difficult to trace and can only be corrected by training and vigilance of personnel (Clarke et al., 1998).

It is important to note at this point that not all the uncertainty or variability of a measurement relates to errors or mistakes on behalf of the monitoring staff. For example there will be normal variability of the process and also limits to the accuracy of measurements and analytical techniques that will contribute to random noise.

A critical element of a quality system is ensuring that the systems of calibration and measurement are traceable to national standards of measurement and that confidence can be placed in the quality of measurements carried out at all steps in the traceability chain (Clarke et al., 1998). Validation is necessary to demonstrate the instrument's response over its full working range. The methodology utilized in this study is an internationally validated method and therefore the traceability of the method can be determined.

In the next section some of the common sources of error according to Clarke et al. (1998) will be discussed.

2.4.1 COMMON SOURCES OF ERROR

2.4.1.1 SELECTION OF THE SAMPLING POSITION

The sampling position or the ideal location is important to ensure that airflow is uniform, especially when sampling for particulate matter. An ideal straight duct is hard to find, and often the location is compromised because of safe access requirements. Many processes in South African industry have not been designed with sampling in mind, and the provision for suitable site access has not been made available therefore the sampling locations in a vast majority of cases do not comply with the minimum requirements as set out in ISO 9096:1992 and 2003.

2.4.1.2 SAMPLING TECHNIQUE

Many sampling techniques utilized for stack sampling may not have been fully validated under field conditions but have been developed from occupational uses where conditions are very different (lower concentrations and ambient temperatures and humidities). Temperature and humidity effects can have a considerable effect on systems, reducing collection efficiency of the absorption technique. It is important to carefully research the background of the method to be utilized. Moreover, it may be necessary to undertake a trial to determine if the methods are acceptable.

2.4.1.3 PROCESS UNDERSTANDING

Many sampling campaigns achieve unrepresentative results as the sampling period chosen does not accurately represent the process emission. It is important to note that many sampling techniques have been developed for relatively steady stack emissions, such as power stations. It is not unusual to have a 100 fold difference in emissions over time periods from 10 months to 10 days. It is important to obtain as much information about the process before commencing any sampling campaign. However, in practice, little data may be available concerning the process as a result of intellectual property and patent rights ensuring that limited information is made available to third parties, such as the test house. For these reasons, process type, variability and continually changing environmental conditions have the greatest effect on the final measurement result obtained as these factors are outside of the control of

the test technician and are part of the random set of uncertainties that are difficult to quantify and account for (Environment Agency Technical guidance note M2, 1993).

Several forces are at play and can account for the unstable flow profile and uneven distribution of particles throughout the gas stream namely:

Saltation - The skipping motion of sand particles forced to move by wind.

Saltation plays a central role in aeolian processes since it usually initiates the other forms of transport, including the emission of dust aerosols that subsequently travel in suspension (Kok et al., 2012). As wind speed increases, sand particles of ~100 μm diameter are the first to be moved by fluid drag. After lifting, these particles hop along the surface in a process known as saltation (Bagnold, 1941; Shao, 2008), from the Latin salto, which means to leap or spring. The impact of these saltators on the soil surface can mobilize particles of a wide range of sizes. This behavior of particles is important in stack emission monitoring as these same forces are at play on the particles in an enclosed off-gas system from an industrial plant and as a result of the uneven distribution of the dust particles in the gas stream necessitates the need for isokinetic sampling.

Indeed, dust particles are not normally directly lifted by wind because their interparticle cohesive forces are large compared to aerodynamic forces. Instead, these small particles are predominantly ejected from the soil by the impacts of saltating particles (Gillette et al., 1974; Shao et al., 1993). Dust particles in enclosed off-gas streams tend to settle on horizontal surfaces, on the duct wall, dampers, fan blades etc. this is important to note as this impacts on the movement and distribution of particles in the off-gas stream. Following ejection, dust particles are susceptible to turbulent fluctuations and thus usually enter short-term (~ 20 - 70 μm diameter) or long-term (< ~20 μm diameter) suspension This is particularly important in an industrial process shortly after start up conditions as the settled dust in the off-gas system will become suspended and entrained in the system by the induced draft fan once it is started. Long-term suspended dust can remain in the atmosphere up to several weeks and can thus be transported thousands of kilometers from source regions (Gillette and Walker, 1977; Zender et al., 2003; Miller et al., 2006). This is especially important in stack emissions as there is usually a large range of particle sizes contained in an off-gas stream. When the regulatory authorities need to determine the impact of the

particulate matter on the receiving environment from a particular emission source it becomes critical to know with some degree of confidence what the particle size distribution is so that long term impacts on health and the environment can be assessed, and how different types, sizes and shapes of particles will impact these aspects quite differently.

The impacts of saltating particles can also mobilize larger particles. However, the acceleration of particles with diameters in excess of ~500 μm is strongly limited by their large inertia, and these particles generally do not saltate (Shao, 2008). Instead, they usually settle back to the soil after a short hop of generally less than a centimeter, in a mode of transport known as reptation (Ungar and Haff, 1987). This is important to note in the context of stack sampling as larger particles may become entrained in the gas stream and may not be emitted into the receiving environment, indeed larger particles if emitted will tend to deposit relatively close to the stack exit due to inertia whereas smaller particles tend to remain suspended in the atmosphere for much longer periods of time and may be deposited several kilometres away from the source as a result of this. Alternatively, larger particles can roll or slide along the surface, driven by impacts of saltating particles and wind drag forces in a mode of transport known as creep (Bagnold, 1937). Creep and reptation can account for a substantial fraction of the total wind-blown sand flux (Bagnold, 1937; Namikas, 2003). The transport of soil particles by wind can thus be crudely separated into several physical regimes: long-term suspension (< ~20 μm diameter), short-term suspension (~20 – 70 μm), saltation (~70 – 500 μm), and reptation and creep (> ~500 μm) (Figure 1.1). Note that these four transport modes are not discrete: each mode morphs continuously into the next with changing wind speed, particle size, and soil size distribution. The divisions based on particle size between these regimes are thus merely approximate (Kok et al., 2012, p. 4-5). The physics of windblown dust is important to note in stack emissions as the particles are removed from the industrial processes effectively by the wind generated by induced draft fans which are responsible for the generation of the flow in most instances. The mechanics of windblown soil/ dust are therefore similar to that of the forces active on the particles contained in an enclosed off-gas stream. Thus as mentioned above the changing gas flow (speed and turbulence) and the particle physical characteristics such as size, shape and density have a great impact on the distribution of the particulate matter emissions being generated from a particular source.

Sedimentation **–** Due to the effects of sedimentation there will invariably be a layer of particulate material on the horizontal surface of a duct and, from this, resuspension may take place causing very variable concentrations (Clarke et al., 1998).To minimize such errors, a length of vertical duct or the chimney itself is preferable to a horizontal section of duct.

Inertial effects – The problem of inertial effects requires that locations close to features that disturb the flow must be avoided (Clarke et al., 1998). The sampling position shall be down stream of any particulate arrestment plant. It shall be located in a straight length of flue, as far downstream as practicable from any obstruction (e.g. bend, fan or damper) that may cause a disturbance and produce a change in the direction of gas flow (BS 3405:1983)

2.5 PRINCIPLES OF MEASUREMENT– SAMPLING ACCORDING TO ISO 9096

There are several international standards for the determination of particulate matter from stationary sources; the more widely used standards are namely:

ISO 9096:1992(E) *Stationary source emissions – Determination of concentration and mass flow rate of particulate material in gas-carrying ducts – Manual gravimetric method*

ISO 9096:2003(E) *Stationary source emissions – Manual determination of mass concentration of particulate matter*

US EPA Method 5, 17: *Determination of particulate matter emissions from stationary sources*

2.5.1 SAMPLING METHODOLOGY

For the purposes of this study the ISO 9096:1992 and 2003 methods will be utilized for the measurement campaigns. These methods have been chosen due to the fact that the ISO9096 method was utilized by Levego for the sampling to produce the data sets that have subsequently been utilized in this study. The abovementioned methods are deemed as equivalent methods by the international measurement community and utilizing either method should produce a similar result. The scientific principles of measurement are effectively the same for all the above mentioned standards with minor differences in approach and application between them.

2.5.1.1 SCOPE OF SAMPLING METHOD EMPLOYED

ISO9096 specifies a manual gravimetric method for the measurement of the concentration and mass flow rate of particulate matter in a moving gas stream in confined spaces such as ducts, chimneys and flues. This method can be used to determine concentrations ranging from 20 mg/m^3 to 1000 mg/m^3. For concentrations under 20 mg/m^3, the inaccuracy of this method will be greater than $\pm$ 10 %.

ISO 9096 is primarily a reference method for the determination of particulate matter emitted from stationary sources the principles of which can also be used for calibrating continuous particulate monitors. The method should be applied as much as possible under steady state conditions of the gas flow duct. It is not suitable for use on ventilation or air conditioning systems, indoor atmospheres, or gases carrying droplets (ISO9096:1992).

It is important to note that if any of the requirements of this International Standard are not fulfilled, the method can still be applied in special cases but the uncertainty on particulate concentration or flow rate may be larger. The uncertainty values if the requirements are not met are not stated in the Standard as there are too many variables to be accounted for. The main purpose for this study is to determine whether the uncertainty can be adequately determined if the minimum requirements of the standard are not met.

2.5.1.2 PRINCIPLE OF SAMPLING METHOD

A sharp edged nozzle is positioned in the duct facing into the moving gas stream and a sample flow of the gas is extracted isokinetically for a measured period of time. To allow for non-uniformity of the distribution of particulate concentration in the duct, samples are taken at a pre-selected number of stated positions in the duct cross-section. The particulate matter entrained in the gas sample is separated by a filter medium, then dried and weighed. The particulate concentration is calculated from the weighed particulate mass and the gas sampled volume. The particulate mass flow rate is calculated from the particulate concentration and the duct gas volumetric flow rate. The particulate mass flow rate can also be calculated from the weighed particulate mass, the sampling time and the areas of the sampling plane and the nozzle opening.

2.5.1.3 SUMMARY OF THE SAMPLING METHOD

A representative gas sample is withdrawn from the source. The degree to which this sample represents the total flow depends on the:

- Homogeneity of the gas velocity within the sampling plane (stable, uniform flow within the enclosed flue system is required). The gas flow in off-gas ducts are such that laminar flow is rarely, if at all, achieved (Hawksley et al., 1977).

- A sufficient number of sampling points in the sampling plane which would depend on the size of the duct or stack (larger sampling plane requiring more sampling points).

- The isokinetic withdrawal of the sample will also have a significant effect on the degree to which the sample is representative of the total flow in the gas stream (Hawksley et al., 1977).

Normally the gas has to be sampled at multiple points within the sampling plane, depending on the sampling plane area. This plane is usually divided into equal areas, at the center of which the gas is withdrawn. To determine the particulate concentration in the plane, the nozzle is moved from one sampling point to the other, extracting gas isokinetically at each point. Sampling periods should be equal for each

sampling point, resulting in a composite sample. If equal sampling areas cannot be chosen, the sampling period shall be proportional to the sampling area.

The number of sampling points is not the only factor affecting the accuracy of a measurement emission. It depends also on the duration of sampling each increment. The reason for this is that the flow of solids at any point is never constant but fluctuates randomly above and below the average value. These random fluctuations are always present even when the plant is being operated under steady conditions (Hawksley et al., 1977, p 5).

The sample is extracted through a sampling train, which principally consists of the following; a sampling probe tube with entry nozzle, a particle separator, in-stack or external, a gas metering system, in-stack or external, and a suction system (Figure 2.1). The particle separator and/or the gas metering system may be either located in the duct or placed outside the duct.

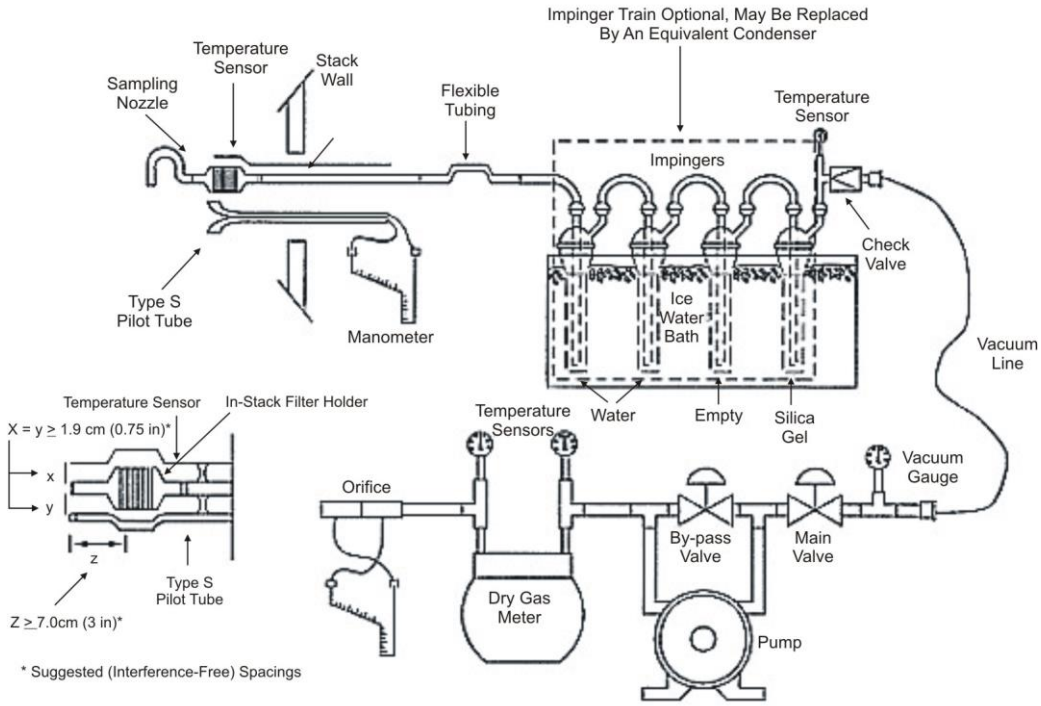

Figure 2.1 Particulate Matter Sampling Train with In-Stack Filter – Source, EPA Method 17

It is necessary to avoid condensation of the vapor (water, sulphuric acid, etc.) in the sampling train during gas sampling, as condensation will interfere with the particle

separation, particulate condition and flow measurement. To this end, the probe tube, the particle separator, and the gas flow measuring device are heated above the relevant dew-point. The water vapor may intentionally be removed downstream of the particle separator, to make use of a dry-gas meter for the measurement of sample gas volume, if the water vapor content of the duct gas does not vary appreciably during sampling.

For isokinetic sampling, the gas velocity at the sampling point in the duct has to be measured and the corresponding sample gas flow has to be calculated and adjusted. Normally, a pitot static tube is used for the measurement of duct gas velocity. The pitot static tube is utilized to measure the static and differential pressures at each equal area inside the gas stream. The stack gas temperature is also measured at each of these points. Together, with an estimation of the gas density (carbon dioxide CO_2 and oxygen O_2 for typical combustion process), these values are used to calculate the velocity profiles and volume of the gas stream present in the stack. If the sample gas flow measuring device is used within the duct, the relation between the measured pressure drop and the Pitot static tube differential is simple, facilitating the adjustment to isokinetic conditions.

If the gas metering device is located outside the duct, the calculation of the isokinetic sample gas flow rate is more complicated. The calculation for isokineticity must also include the duct gas density under standard conditions (which may be derived from the dry gas composition and the moisture content). The temperature and static pressure of the gas in the duct and the gas metering device must also be noted if the sample gas flow is measured after water removal.

After sampling, the collected particulate matter is completely recovered (which can necessitate cleaning of the probe and nozzle), dried and weighed. It is important to note that the filter utilized for the separation of the particulate matter from the gas stream must undergo preconditioning, where it is dried cooled and weighed. The same filter conditioning is applied after the sampling is completed. The difference between the post-weight and pre-weight of the filter will be representative of the mass of the particulate matter collected from the gas stream.

2.5.2 CLASSIFICATION OF SOLIDS/PARTICULATE

The nature of solids contained in the waste flue gases from combustion appliances consist of three types of material These materials are derived in different ways and found in different proportions according to the kind of appliance and the type of fuel;

- Fly-ash consisting of incombustible particles derived from minerals associated with the fuel,
- Chars or cokes, consisting of partially burnt or carbonized particles and fuel,
- Carbon particles formed in the course of gas-phase combustion of volatile hydrocarbons

The particles of different types, although found separately as discreet particles, often occur as mixtures, sinters, aggregates and agglomerates. They differ in the ranges of particle sizes that permit the classification into grit, dust and soot. The composition and particle size of the solids carried out of the combustion chamber depend on the type of appliance, the method of combustion, the nature of the coal and its mineral constituents, the furnace temperatures, gas velocities, and the efficiency of combustion (Hawksley et al., 1997).

It is important to have an adequate definition of total suspended particulate matter and understand the broad categories the various particles are classified under, and how they affect the accuracy of the sample obtained. To this end, the following broad classification of solids emitted from typical combustion processes is defined by (Hawksley et al., 1997, p 34):

Since the behavior of solids in gases is determined predominantly by their size (strictly, their terminal velocity), it is preferable to distinguish them by the size classes of grit, dust and soot rather than as chars, fly-ash and carbon particles.

Grit is defined as solid particles retained on a 200 BS mesh sieve, which has a normal aperture of 75μm. Grit consists chiefly of chars but may also include some fly-ash either as separate entities, usually in the form of loose easily dispersed flocs, or as agglomerates of sintered chars. Grit that consists of partially burnt or coked fuel –

dark grey to black in color – is resistant to breakage, but grit that is composed of aggregates of ash particles – light grey to white – may be very friable. The bulk density is about 500kg/m^3. Grit particles can easily be seen individually with the naked eye, and have an average density of about 1000 kg/m^3. They have terminal velocities in air greater than 150mm/s, and consequently are easily removed by simple types of gas cleaning plants. Some systems used to remove grit particles are settling chambers or centrifugal grit arrestors, the particles tend to be deposited on the floors of horizontal flues, and when emitted from the chimney, they fall in the immediate neighbourhood.

Dust is defined as solid particles smaller than 75 µm and larger than about 1µm. Dust is composed mostly of fly-ash but may include also some chars and occasionally large flocs of carbon particles derived from deposits on the walls of the flue. Its colour ranges from a reddish brown through light grey to darker shades. The bulk density is about 1000kg/m^3. Dust particles can be seen with the aid of a microscope. The density of the individual particles varies widely from 100kg/m^3 (hollow spheres) to about 5000 kg/m^3 (solid iron oxide particles), however most dust particles have an average particle density of 2000-2500kg/m^3. They have terminal velocities ranging from 1/20 to 300mm/s. Dust particles, at least down to sizes of 10 - 20 µm, can be removed by any efficient type of mechanical collector; in practice, many cyclones are not adequately efficient owing to poor maintenance, inefficient operation or bad design. Dust particles emitted from a stack are deposited over distances ranging from a few hundred metres to many kilometres from the stack. This is specifically relevant to the South African context where many of the coal fired power stations in the country are significant contributors to particulate matter emissions. This is because they are emitted at a relatively high altitude in terms of stack height (approximately 300m above ground level on average on the south African Highveld) in order to ensure emissions are emitted above the inversion layer, and to ensure maximum dilution. It is thus not unusual to find that dust emissions are deposited over vast distances of up to several kilometres.

Soot is defined as solid particles smaller than 1µm. Soot consists mainly of carbon particles, but may also include condensed particles and some tarry matter and perhaps some fly ash. Soot is black in color, packs loosely, and generally has very low bulk density. Soot particles are sub microscopic and cannot be seen individually under the

microscope. The particles have a strong tendency to aggregate into too chains or threads, perhaps as much as a few microns in length, but so thin that they behave aerodynamically as if sub-microscopic in size. The density of individual particles is about 2000 kg/m^3. They have terminal velocities smaller than 1/20 mm/s. Soot cannot be removed from flue gases except by means of filters or electrostatic precipitators, and when emitted from a stack, the bulk will remain in suspension in the atmosphere until washed out by rainfall or carried to the ground at great distances – hundreds of kilometres from the stack – by the slow process of diffusion.

A small amount of soot, like gaseous pollutants, does of course reach the ground, by diffusion, at distances of only a few stack heights. Soot particles by virtue of their sub-microscopic size, have a high light-obscuring power and are mainly responsible for the visible appearance of 'smoke' from chimney stacks. A further important point is that soot particles are usually very well mixed with the flue gases so that their concentration tends to be the same at all points over the cross-section of the flue.

2.6 STATISTICAL METHODOLOGY: A CRITICAL REVIEW

The approaches to calculating method uncertainty utilized in the "Guide to the Expression of Uncertainty in Measurement" (generally known as GUM, 1995) are the underpinning methods utilized for analysing the data sets under review. In general, the concept of measurement uncertainty as described in the GUM has been broadly accepted by the measurement community (Robinson, 2004).

The viewpoint of GUM is that all the components that make up the uncertainty of measurement are of the same nature and are to be treated identically. As a starting point for discussions, a simplified derivation of the mathematical expression for the propagation of standard deviations is utilized, termed in the guide the law of propagation of uncertainty. It is important at this point to define what is meant by the term uncertainty. The formal definition of the term uncertainty of measurement developed for use in terms of GUM may be defined in two ways as follows: "The word uncertainty means doubt, and thus in the broadest sense the "uncertainty of measurement" means doubt about the validity of the result of a measurement." (GUM, 1995, p 2)

“Uncertainty is the unknown (of measurement) parameter, associated with the result of a measurement, which characterizes the dispersion of the values that could reasonably be attributed to the measurand (value of a quantity).” (GUM, 1995, p 2)

From these definitions, the parameter may be for example a standard deviation (or a given multiple of it). Uncertainty of measurement, in general, comprises of many components. Some of these components may be evaluated from the statistical distribution of the results of series of measurements and can be characterized by experimental standard deviations (Figure 2.2). The other components, which also can be characterized by standard deviations, are evaluated from assumed probability distributions based on experience or relevant information; for example one can assess the quality of data on adherence to the minimum requirements of a specific standard. If certain of the requirements are met, then one can make specific assumptions about the data. The author has utilized this statistical method and applied the principles to both sets of data utilized for the study.

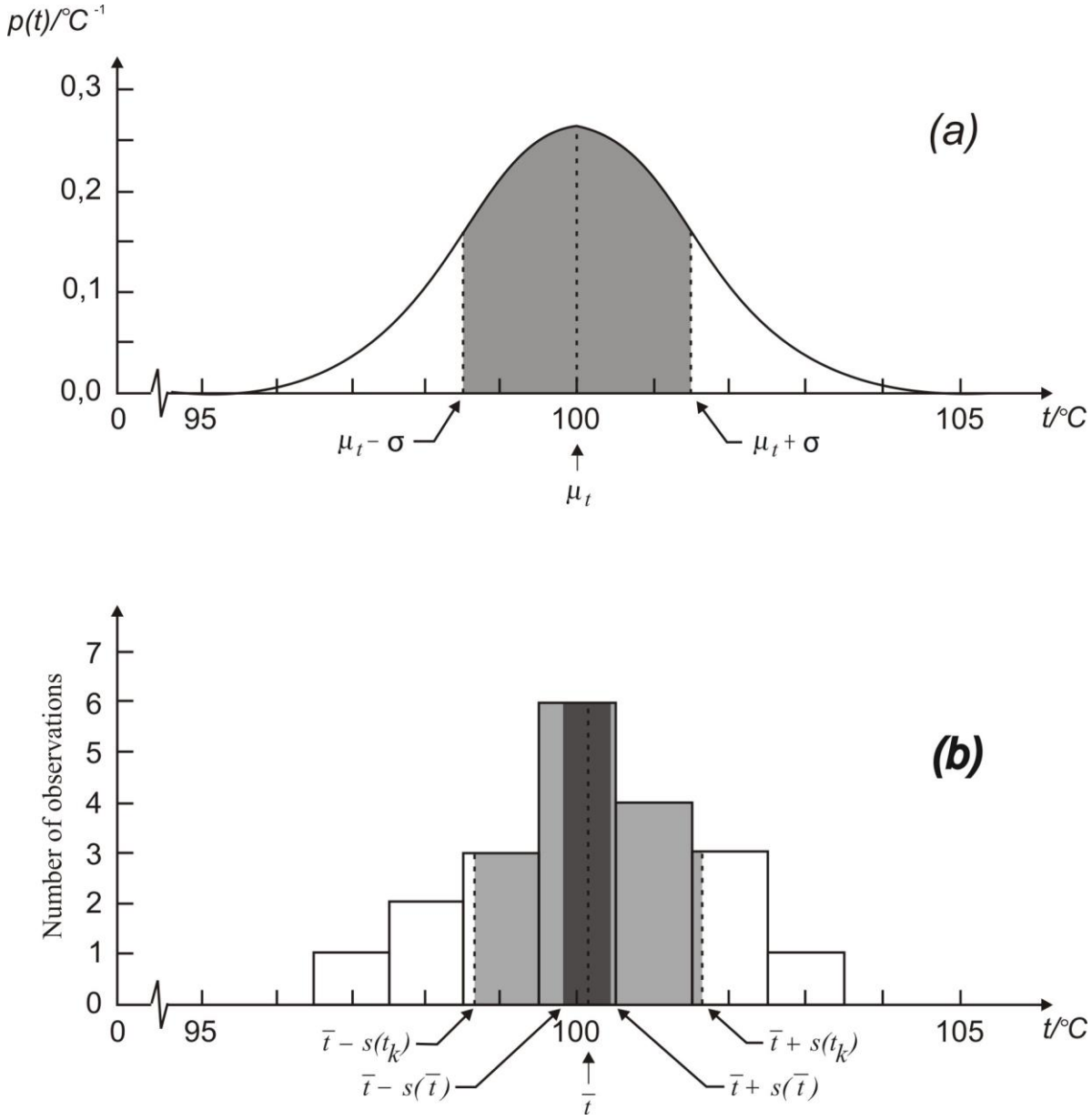

Figure 2.2 Graphical Illustration of evaluating the standard uncertainty of an input quantity from repeated observations (Source; GUM, 1995).

It must be understood that the result of the measurement is the best estimate of the value of the measurand, and that all the components of uncertainty, including those arising from systemic effects, such as components associated with corrections and reference standards, contribute to dispersion (GUM, 1995).

The objective of a measurement is to determine the value of the measurand, which is the value of a particular quantity to be measured. A measurement therefore begins with an appropriate specification of the measurand, the method of measurement, and the measurement procedure. In general, the result of a measurement is only an approximation or estimate of the value of the measurand, and thus is complete only when accompanied by a statement of the uncertainty of that measurement (GUM, 1995).

In many cases, the result of a measurement is determined on the basis of a series of observations obtained under conditions that are repeatable. Variations in repeated observations are assumed to arise due to the inconsistency of the influence quantities that can affect the measurement result.

It is important to distinguish between repeatability and reproducibility in conducting a series of measurements and in ultimately determining the final outcome and interpretation of the results obtained.

- Repeatability: measurements taken under the same conditions where the variables and uncertainties are kept consistent.
- Reproducibility: The attempts to reproduce the results of the repeated observations under differing or varying conditions.

Table 1: Repeatability vs. Reproducibility

Repeatability	**Reproducibility**
Same sample	Same sample
Short time	Over a considerable period of time
Same operator	Different operators
Same equipment	Different equipment
Same method	Different methods

Source; NLA uncertainty of measurement short course 20 – 24 June 2011

In general, a measurement has imperfections that give rise to an error in the measurement result. Traditionally, an error is viewed as having two components; a random component and a systematic component. It is important to note that error is an idealized concept and therefore errors cannot be known exactly (GUM, 1995). Random error presumably arises from unpredictable or stochastic temporal and spatial variations of influence quantities. Although it is not possible to compensate for the random error of a measurement result, it can usually be reduced by increasing the number of observations. In GUM, it is highlighted that great care is used to distinguish between error and uncertainty. They are not synonyms, but represent completely different concepts; they should not be confused with one another or misused.

Systematic error, like random error, cannot be eliminated but it too can be reduced. If a systematic error arises from a recognized effect of an influence quantity on a measurement result, hereafter termed a systematic effect, the effect can be quantified and if it is of significant size relative to the required accuracy of the measurement, a correction factor can be applied to compensate for the effect (Figure 2.3).

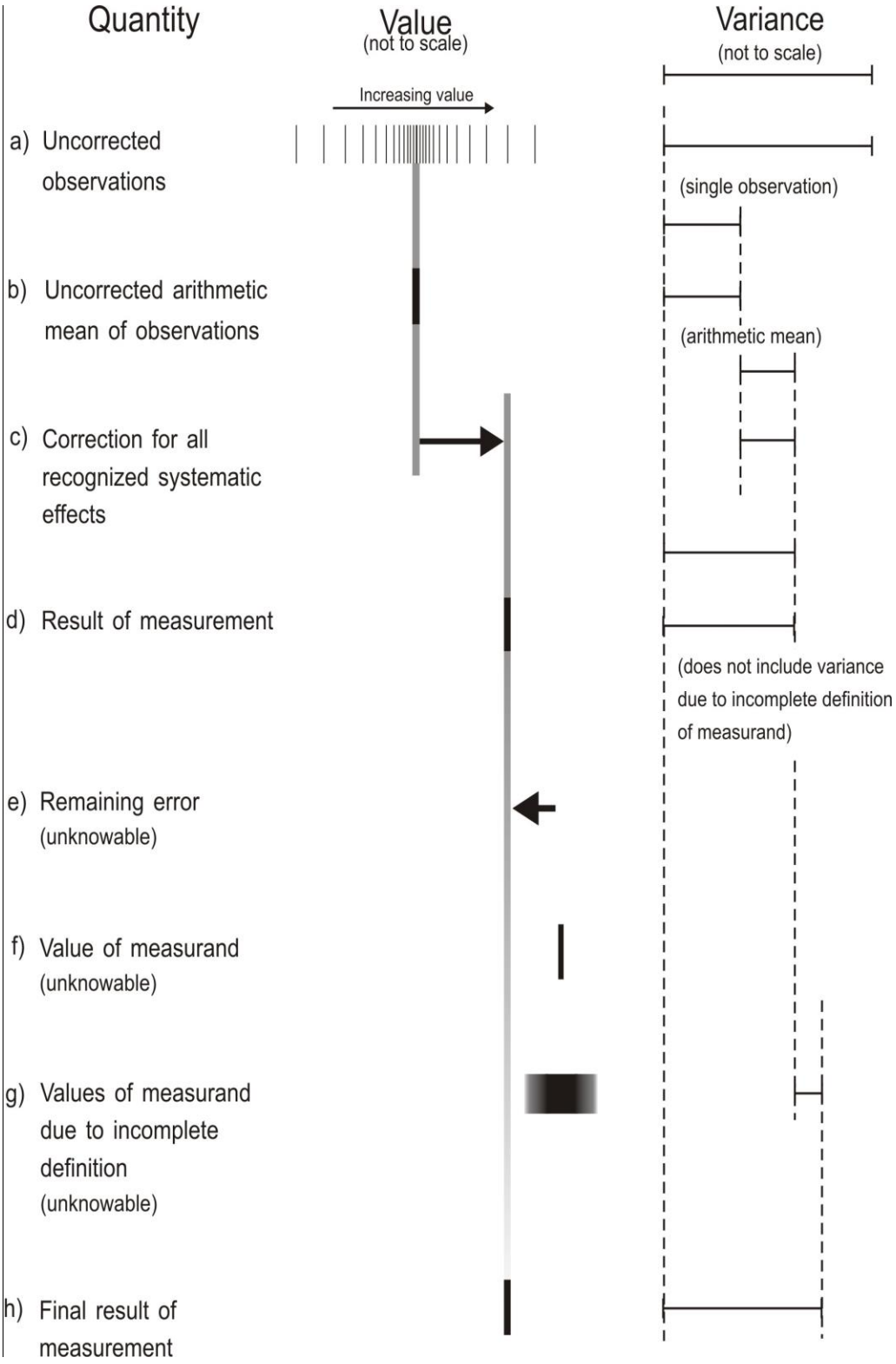

Figure 2.3 Graphical illustrations of values, error and uncertainty (Source, GUM, 1995)

The uncertainty of the result of a measurement reflects the lack of knowledge of the results of the measurand. The results of a measurement after recognized systematic corrections are applied is still only an estimate of the value of the measurand because

of the uncertainty arising from random effects and from imperfect correction of the result for systematic effects.

In practice, there are many possible sources of uncertainty in a measurement (GUM, 1995), including:

- *Incomplete definition of the measurand;*

A question that must be raised is the degree of precision of the definitions used in the measurement process. Enough exact knowledge of the value of the measurand is unavailable. All measured components are not absolute; they all have uncertainties with regards to the value obtained. For example, if the particulate matter concentration of a gas stream is measured, what constitutes particulate matter? Is the value obtained reported on a wet basis or a dry basis? If the measured components are not properly defined or if there is not enough information in order to express the results correctly, a satisfactory answer may not be obtained.

- *Non-representative sampling - the sample measured may not represent the defined measurand;*

The measurement device or sampling train operator may not take into consideration all the variables that may influence the accuracy of the sampling and thus result in non-representative sampling. For example, if the operator does not take moisture in the flue gas stream into consideration, a significant error on the sampled volume may occur.

- *Inadequate knowledge of the effects of environmental conditions on the measurement or imperfect measurement of environmental conditions;*

The effects of ambient moisture and temperature as well as turbulence (strong winds) may all have effects on the final result but may not be quantifiable.

- *Personal bias in reading analog instruments*;

Human error, variables outside of the control of the operator, may in some instances have a major effect on the final value obtained. Many constants and assumptions are not always applicable in certain calculations and have to be considered when trying to obtain a representative value for the measurand. When reading an inclined

manometer, the readings fluctuate and the actual readings noted by the operator are subjectively biased in accordance with the operator's interpretation of the reading.

- *Finite instrument resolution or discrimination threshold;*

The refinement of the instrumentation utilized in the sampling train may have a major effect on the results. For example, if the operator utilizes an inclined manometer and Pitot tube to measure pressures within an enclosed flue system, there will be limits of detection for the scale. In other words, if the measurement parameter being measured is not within the exact range of the instrument, one may not get an accurate reading or one may not get a reading at all.

- *Inexact values of measurement standards and reference materials*;

If instruments or standard reference materials that do not meet the minimum requirements of a set standard are utilized, it could introduce uncertainties greater than those stated in the standard (e.g. utilising a weighing balance for the determination of filter mass that does not adhere to the minimum requirement of the standard).

- *Inexact values of constants and other parameters obtained from external sources and used in the data reduction algorithm;*

This is a case in point, especially when modeling stack plumes, assessing health and environmental impacts and permit compliance etc. Because it is not always possible or feasible to measure every component in the atmosphere- such as wind direction, inversion layers etc. Incorporation of stability constants based on educated assumptions or prevailing weather conditions may need to be considered, which in certain circumstances give completely wrong information to the model, and therefore the model predictions will not be remotely close to the real values on the ground or in the field.

- *Approximations and assumptions incorporated in the measurement method and procedure*;

Wrong assumptions and approximations do not always hold true, especially if the conditions under which the sampling takes place are extreme conditions and push the limits of the relevant standard.

- *Variations in repeated observations under apparently identical conditions;*

This may result from the limitations of the instrumentation being utilized in the sampling. For example, the control unit device used in isokinetic sampling may be manually operated which means that between different supposedly "ideal" conditions, slight differences may occur in the way the control valves are operated, which will give rise to variations in the values obtained even in seemingly "ideal" conditions. It is important to bear in mind that so-called "ideal" conditions do not readily occur in the field due to the number of variables accounted and not accounted for.

There are two methods utilized in GUM for evaluating the uncertainty of a measurement. The uncertainty of a correction for a known systematic effect may, in some cases, be obtained by a Type A evaluation while in other cases by a Type B evaluation.

The purpose of the Type A and B classification is to indicate the two different ways of evaluating uncertainty components; this distinction is for convenience of discussion purposes only. The classification is not meant to indicate that there is any difference in the nature of the components resulting from the two types of evaluation. Both types of evaluation are based on probability distributions and the uncertainty components resulting from either type are quantified by variances or standard deviations.

The estimated variance characterizing an uncertainty component obtained from a Type A evaluation is calculated from a series of repeated observations and is the familiar statistically estimated variance. The estimated standard deviation, the positive square root of the variance (see equation 1), is for convenience sometimes called a Type A Standard uncertainty (Figure 2.4).

(1)

$$s_D = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left(D_i - \overline{D}\right)^2}$$

Source: prEN 14181 Quality assurance of AMS, p 19.

For an uncertainty component obtained from a Type B evaluation, the estimated variance is evaluated utilising available knowledge, and the estimated standard deviation is sometimes called a type B standard deviation (Figure 2.4).

Thus, a Type A standard uncertainty is obtained from a probability density function derived from an observed frequency distribution, while a type B standard uncertainty is obtained from an assumed probability density function based on the degree of belief that an event will occur (often called subjective probability). Both approaches employ recognized interpretations of probability. A type A uncertainty utilizing an observed frequency distribution was utilized by the author for this study.

Given the complex nature and the unknowns associated with sampling in the field due to systematic and random effects, the author has chosen to simplify the investigation by assuming that the systematic errors are within the method specifications for both Source A and B sampling campaigns. Random Uncertainties – these give rise to a variation about the mean and tend to exhibit a Gaussian or similar statistical distribution. A degree of confidence may be assigned to the mean of the measurements, therefore increasing as more samples are taken. Typically random uncertainties arise from small variations in procedure and may be controlled by accurate specification of procedures and by training the operators to ensure that these procedures are followed rigorously (Clarke et al., 1998).

Systematic uncertainties – these introduce a bias into the measurements and do not vary about the mean. These can be reduced by ensuring the use of appropriate equipment, insisting on regular calibration and implementing a regular program of maintenance. Systematic uncertainties also arise from differences in sampling practice between operators. These latter uncertainties are the most difficult to trace and can only be corrected by training and vigilance of personnel (Clarke et al., 1998).

The effect of the above assumptions is that there is enough data to allow for statistical analysis to be conducted and determine the variability and standard deviation for the data set obtained. If there is not enough data obtained then the subsequent variability and standard deviation of the measurements obtained maybe appreciably large and therefore any inference from the results will be deemed meaningless.

If the systematic uncertainties such as bias, use of uncalibrated equipment and training of the personnel etc. is not addressed adequetly could lead to errors in the results not being accounted for as the assumption is that all equipment is calibrated and the training of personnel is of a required minimum standard and will in turn reduce the bias in the results obtained.

It is also assumed that these systematic errors have a small effect (when controlled adequately) on the reproducibility of the measurements when compared to the errors obtained from random effects encountered in the field as these systematic errors can be controlled and adequately accounted for. Source A is defined as fully compliant and the relevant errors and specifications of the standard have been utilized. For the non-compliant Source B, the process specifications set out in the standard do not comply (specifically noncompliance of the sampling location requirements), and hence a comparison on the effect of non-compliance to the sampling location can be ascertained.

The most appropriate approach for the purposes of this investigation into determining the uncertainty of stack emissions will therefore be to utilize the Type A approach, as defined in the GUM. The uncertainty of measured emissions will thus be calculated from a series of repeated observations obtained from the data sets for Source A and Source B sampling campaigns (samples conducted by Levego utilizing ISO9096).

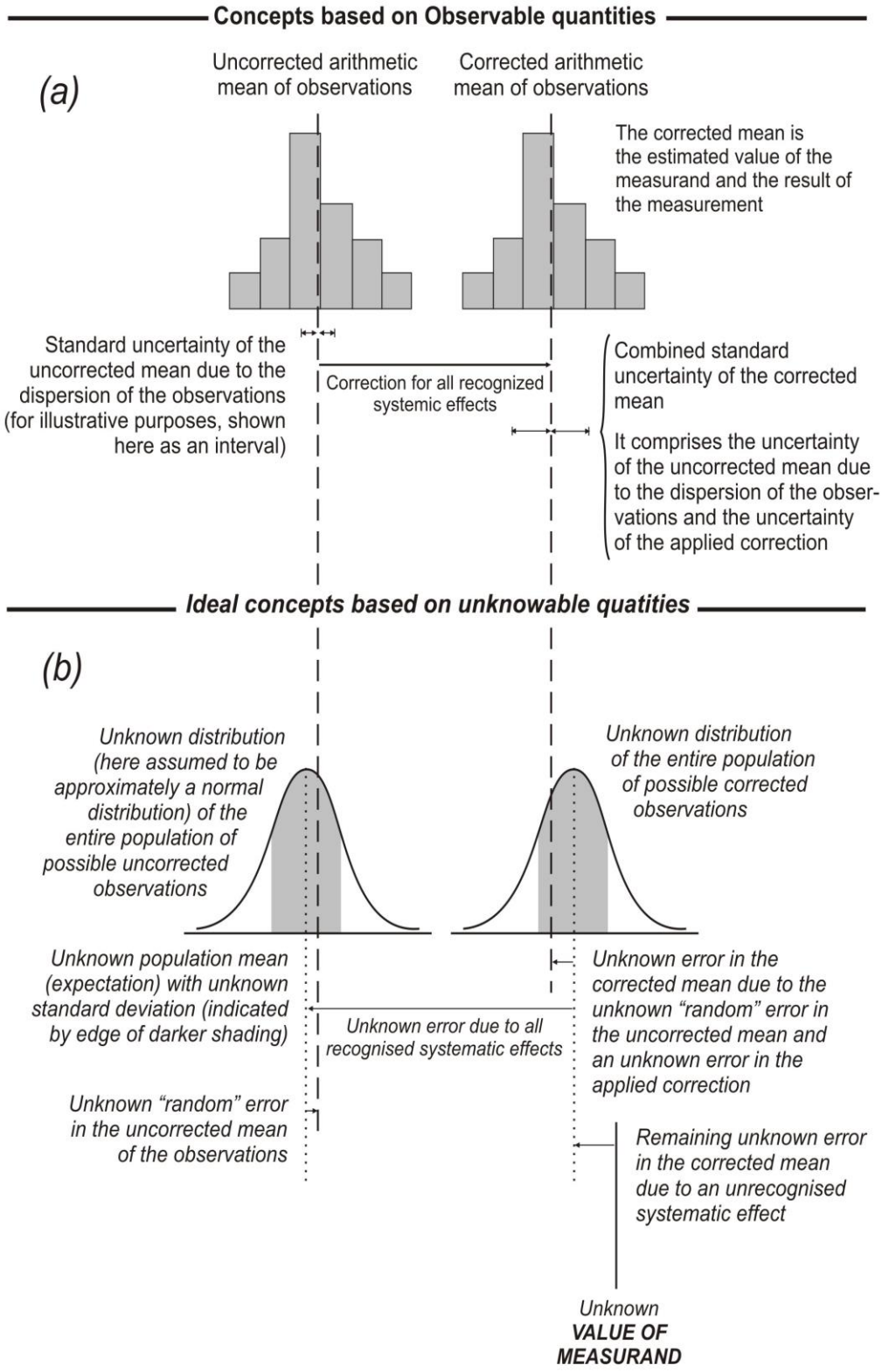

Figure 2.4 Graphical illustrations of value, error and uncertainty (Source; GUM)

CHAPTER 3: EXPERIMENTAL COMPARISONS

3.1 OVERVIEW OF APPROACH

Two sampling campaigns for the determination of concentration and mass flow rate of particulate matter were conducted (see section 2.1). The results from both sampling campaigns have been included (see section 4) and evaluated in order to determine the greatest source of error contributing to the uncertainty of each component, which in turn contributes to the overall uncertainty of the final reported results from each sampling campaign.

3.2 COMPLIANT VERSUS NON-COMPLIANT SCENARIOS

ISO 9096:1992 and 2003 stipulates certain minimum requirements to be adhered to in order for the final measurement results to comply with the measurement inaccuracy of approximately 10 % for the final results reported as set out in the standard. The minimum requirements set out in the standard were utilized as the basis for determining the compliance and non-compliance of each sampling campaign. The minimum requirements are set out into three categories as follows; sampling location, equipment for dust collection and equipment for determining flue gas characteristics.

The non-compliance of the sampling location to the minimum requirements is assumed to be the single biggest contributing factor to the uncertainty in the measurement result (see section 2.2). This is deemed to be the case as the sampling equipment and the equipment utilized for the flue gas characterization is in control of the sampling specialist. The subsequent laboratory analysis of the samples, are carried out under controlled laboratory conditions (which include corrections for temperature humidity and pressure) and thus have minimal impact on the error associated with the final result reported.

Sampling equipment compliance is obtained by ensuring the use of equipment that complies with the relevant accuracies required by the standard for each component of the sampling train (see Table 3.1). The use of relevant approved instrumentation and

the calibration of equipment on a regular basis will ensure that the equipment is adequate to adhere to the requirements of the standard.

The sampling location, however, is out of the control of the sampling specialist. From the author's extensive experience obtained from conducting thousands of sampling campaigns on various processes, it has been found that the non-compliance of the sampling location has been noted as the major source of uncertainty in the majority of surveys conducted

For the purposes of this study, a compliant stack (Source A, See section 4.4) is deemed to be a sampling campaign that has fulfilled all the minimum requirements as set out in the method 3. A non-compliant (Source B, see section 4.5) scenario is one in which the sampling location has fulfilled all the minimum requirements as set out in the method and only the sampling location requirements have not been fulfilled.

Sampling can be conducted either cumulatively or incrementally, both have advantages and disadvantages as per Hawksley et al. (1977, p 5). The cumulative method may be slightly quicker and might be preferred by the experienced operator for routine testing (Hawksley et al., 1977). It becomes necessary to collect the sample in increments taken from a number of points due to solids not being distributed uniformly over the cross-sectional are of the flue. The increments may be measured separately at each point and the average weight calculated from the separate. Or a single gross sample may be collected by moving the sampling nozzle from point to point - termed cumulative sampling. It is sufficient to note that the incremental method is recommended for the beginner because it is easier to spot mistakes, it is also the method preferred by the research investigator since it gives information on the reliability of the average. However the cumulative method has been utilized for this study as the data were obtained from commercial compliance sampling campaigns which are extremely expensive to conduct. The cumulative method deemed by the author to be sufficiently accurate for the purposes of this study as the time and costs involved have limited the use to cumulative sampling. For future campaigns incremental sampling may be useful since it may give information regarding the reliability of the mean, this has not been the focus of this project and therefore has not been conducted.

Table 3.1 Summary of requirements – Apparatus and sampling conditions as per ISO: 9096:2003

SAMPLING LOCATION	Approx. Value
Flow angle	$<15^{o}$
Pressure difference (pitot tube)	> 5 Pa
Ratio of max gas velocity to min gas velocity	3:1
Negative flow	None
Straight length before the sampling plane	> 5 hydraulic diameters
Straight length after the sampling plane	> 2 hydraulic diameters
straight length before emission point	> 5 hydraulic diameters
Number of sampling points	dependant on duct size
EQUIPMENT FOR DUST COLLECTION	
Alignment of the nozzle	10%
Isokinetic Criteria	+15% and - 5 %
Leak test	<2%
Condenser, drying tower: residual gas moisture	$< 10\ g/m^3$
Gas meter volume measurement uncertainty	2%
Absolute pressure measurement uncertainty	1%
Absolute temperature measurement uncertainty	1%
filter efficiency (test aerosol 0,3um)	> 99.5 %
Filter material (adsorption of components)	No reaction or adsorption
Nozzle straight length before the first bend	> 30 mm
Nozzle tip: distance to obstacles	> 50 mm
Nozzle: Length with constant internal diameter	>10mm
Nozzle: variation in diameter angle	$< 30^{o}$
Nozzle Internal diameter	>4mm
Nozzle area: measurement uncertainty	10%
Elbow: Radius of the bend	> 1,5 *d*
Balance resolution (mg)	0.01mg to 0.1mg
weighing uncertainties	<5% of the LV for process
Thermal stability (filter)	>8h
Overall Blank Value	<10% LV or 2 mg/m^3
Sampling time measurement uncertainty	5secs
linear measurement uncertainty	1% duct .2mm / 5% Nozzle
EQUIPMENT FOR FLUE GAS CHARACTERISTICS	
Absolute temperature	1%
Flue gas density	0,05 kg/m^3

3.3 DISCUSSION

Compliance to the minimum requirements of ISO9096:1992 and 2003 is critical in ensuring good data quality. Table 3.1 illustrates all the major components that have an impact on the sampling accuracy. A compliant sampling location is critical in obtaining good data (refer to Section 2.2). One can ensure that all the sampling equipment utilized is compliant and the sampling train operators are adequately trained and still have questionable results as a consequence of a poor sampling location.

At this juncture it is critical to emphasise why an appropriate sampling location is so important. The sampling for particulate matter is done isokinetically (see Section 2.3). This means that a sample is taken at a number of predetermined equal area points within an enclosed flue gas stream. At each point, the velocity is measured and the sample rate adjusted accordingly in order to sample at the flue gas rate for each point. The positioning of the sampling location is critical in ensuring that the most stable, uniform flow of gas in the gas stream is obtained. This is to minimize the adjustments that are needed to control the gas sampling device to ensure isokinetic conditions are maintained for the duration of the test. Therefore, if one has turbulent flow of the gas stream, much greater adjustments need to be made to ensure the isokineticity of the sample; these adjustments result in a greater error being contributed to the overall uncertainty of the measurement. The greater the adjustments needed to maintain isokineticity, the larger the contribution to the overall uncertainty of the final result.

It is important to be aware of the performance characteristics that are expected of a method or standard. The Environment Agency of the United Kingdom has stipulated measurement uncertainties that need to be adhered to for each of the main pollutants listed in the table below. It is important to note that these uncertainties are reported as expanded uncertainties at a 95% confidence interval. It is interesting to note that the required uncertainty for dust is 30%; the results from this study has obtained a 62 – 73% uncertainty which is more than double the requirement of these directives. These requirements are referenced in the study as these directives have been adopted by the European Committee for Standardization (CEN) and highlights the fact that the data sets utilized in the study are too small.

Table 3.2 Measurement Uncertainties specified by the Waste Incineration Directive(WID) and Large Combustion Plant Directive(LCPD)

Pollutant	95% confidence interval
Total dust	30%
TOC	30%
HCl	40%
SO_2	20%
NOx	20%
CO	10%

Source: WID and LCPD

3.3.1 CRITICAL FACTORS AFFECTING THE ACCURACY OF SAMPLING

The average mass flow or concentration determined by sampling over a certain period may differ from the actual mass flow in that period for a number of reasons stated below according to Hawksley et al. (1977, p42).

i. Effect of number of sampling points utilized

The mass flow per unit is (m_i) at the selected sample area may not be equal to the average for the whole sub-area A_i. Since the mass flow or concentration per unit area changes from point to point across the flue in a manner that is not known before hand, it is not known which particular point in a given sub-area corresponds to the position where the mass flow per unit area has the average value for the sub-area (that is, when the pattern of flow can be represented by an inclined plan surface), the mass flow per unit area (m_i) at a sample area located at the centre of the sub-area will correctly give the average mass flow through the whole sub-area. This will clearly be the case however variable the mass flow may be over the whole area of the flue, if the sub-areas are sufficiently small; that is if the number of sampling points is sufficiently large. Conversely, the fewer the number of sampling points, the greater the chance the

measured mass flow or concentration will differ from the true value. The magnitude of the error depends on the given number of sampling points utilized, the complexity of the pattern of mass flow in the gas stream, or the particulate matter concentration present in the flue gas.

Fortunately, although the pattern of mass flow may be of a complex nature on a detailed scale, it is usually relatively simple in broad outline, with the mass flow or concentration falling to lower values near the walls from a single region of high flow. Consequently, it has been found that a fairly small number of sampling points are sufficient. There is little improvement in accuracy to be gained by using more than 16 sampling points, and even with as few as four points, the error is not likely to be more than about 15% in most cases. The error arising from the use of a finite number of sampling points is a systematic bias (either positive or negative) which cannot be reduced or eliminated by repeating the measurements at the same set of sampling points.

ii. Effect of plant conditions during sampling.

If the distribution of mass flow is uniform across the flue, and the sampling is carried out for the same duration for each increment ($t_1 = t_2 = t_3 \ldots$), and without intervals between successive increments, the average mass flow or concentration during the sampling period is obtained accurately and without error, no matter how great the variability of the mass flow with time. In practice however, the distribution is not uniform and there is also no systematic error in the measured mass flow or concentration. There are of course exceptions to this, for example when the measurement is taken at points of high mass flow or concentration and at times when the average flow is high or at points of low flow with low average flow. Practical experience has shown that the error from an accidental correlation is in general negligible in comparison with other sources of error. The important practical conclusion which has not in the past been generally appreciated is that there is no need to maintain steady conditions of solid (or flue gas) flow when measuring the average emission. This is fortunate because in the case of the smaller boiler plant it is often impractical to do so. The practical considerations taken during sampling was to confirm with the plant personnel that the plant was operating under stable conditions,

this may still include natural variation in the process but as mentioned above this variation will have a negligible effect on the results obtained.

iii. Effect of sampling velocity:

A systematic error arises if sampling is not isokinetic. The difference between velocity of suction into the sampling nozzle, and the velocity of the flue gases at the sampling point, results in a difference between the weight of solids actually entering the nozzle and the weight flowing through the sample area - as defined by the nozzle. When the two velocities are equal, the flow lines are undisturbed and the solids are not deviated from their path. If the suction is too high, solids that would not have passed through the sample area are drawn into the nozzle, whilst if the suction velocity is too low, some solids that should enter the nozzle will fail to do so. The errors associated with this scenario are small for grit (coarse particles) as they tend to follow their original path due to their inertia; similarly very fine soot particles behave more like gaseous particles and tend to follow the deflected gas stream. A corollary to this is that soot particles will usually be dispersed by turbulence, uniformly over the cross-sectional area of the flue, so that its concentration (but not its mass flow) is the same at any point. The presence of dust particles in the flue necessitates the need for isokinetic sampling in order to obtain an accurate sample.

iv. Effect of sampling duration:

Another error arises from the limited time available for sampling at each point. Although when viewed as an average over a long period of time, the pattern of flow is stable however the mass flow fluctuates widely from instant to instant at any point in the cross section of the flue. Snap samples of short duration taken at points covering the area of the flue would show little evidence of a definite pattern and a repeat set would give a different pattern. The fluctuations appear to be random in magnitude and pattern.

In consequence of these inherent fluctuations, each increment making up the sample is subject to a random error, which is appreciable for the usual durations of sampling (about 5 – 10 minutes per increment) and sample areas (1/1000-1/5000m^2), and amounts to something of the order ±20%. The error in the measurement of the mass

flow is smaller, since the errors for several increments being random tend to cancel each other. The error is in the order of ±10% for a sample composed of four or five increments and ±6% when there are eight or nine increments.

It must be emphasised that this random error is characteristic of the suspension of solids in a turbulent fluid and cannot therefore be eliminated by maintaining steady boiler operating conditions. Fluctuations in emission due to unsteady boiler operation, etc. affect all the sampling points simultaneously and, as discussed above, if the proper sampling procedure has been adopted the resulting systematic error is negligible. The inherent error at each sampling point may be somewhat larger when the emission is unsteady but the available evidence does not support this supposition.

v. Accuracy of Mass Flow Measurement

The accuracy of a measurement of mass flow rate is to a large extent determined by the length of the sampling period over which the average mass flow is to be determined. For a given length of sampling period and number of increments, the overall error (random plus systemic) is least if each increment is collected from a different sampling point and greatest if all the increments are taken from a single point.

vi. Repeat Measurements:

A true repeat measurement of the average mass flow or concentration in a given sampling period can only be carried out by making a simultaneous measurement with a second set of equipment. Such a test would give a measure of the reproducibility but would not disclose whether both measurements were subject to a systematic error due to a particular choice of sampling points, which could only be established only by repeated sampling at other points.

vii. Place and Occasion of Sampling

The choice of the period over which sampling is to be carried out and of the position in the flue system where the measurement is to be made, are both governed more by practical considerations than by theoretical requirements. The minimum duration of sampling should not be less than 3 minutes per point to avoid sampling errors in

timing the duration. The duration should also be sufficient to collect not less than 150mg in order that the errors of collecting and weighing the solids should be tolerably small. In addition the maximum duration of sampling without changing the filter medium should be such that the weight collected does not exceed the capacity of the filter or hopper utilized.

Often the circumstances of obtaining data at the site leave a researcher little choice in sampling points. Sometimes a balance has to be struck between the cost of making access holes at a conveniently accessible sampling position and the cost of providing a temporary working platform to reach a less accessible position where access holes can be more readily cut in the walls of the flue. One of the main limitations of the position of the sampling location is the requirements that the directions of flow of solids and flue gases should be more or less parallel to the axis of the flue and perpendicular to the plane of sampling (Hawksley et al., 1977, p 67).

There are several obstructions namely; bends, dampers, fans etc. that can affect the stability and the uniformity of the flow. In practice the best position for sampling in the majority of cases is in the ducting before the induced draft (i.d.) fan. The optimal position is not closer than one diameter to the fan's inlet.

One of the main problems in a flue stack is that of helical flow. This is when gases flow from a smaller flue into the side of a larger one if the flow is displaced off-axis; this often occurs when an i.d. fan discharges slightly off centre and at high velocity into the base of the stack (Hawksley et al., 1977, p 68).

It should be noted that a reliable estimate of the flue gas volume flow cannot be obtained unless the measurements are made at a distance of several flue diameters, preferably five or more, from upstream bends or other disturbances. In consequence, the concentration cannot be measured as reliably as the mass flow (except in the case of soot).

Although it has been stated that the accuracy of the sampling is not much dependent on the complexity of the pattern of solid flow, it is nevertheless the case that the systematic error will be smaller, for a given number of sampling points, if a sampling position is chosen where the solids are more uniformly distributed over the cross-

section of the flue. Preference should always be given to a sampling position that is furthest from upstream bends and disturbances. Preference should also be given to a sampling position in a vertical flue, since especially for solids containing much grit; the distribution is more likely to be uniform and symmetrical than in the case of a horizontal flue.

A number of practical details should be taken into consideration when selecting a sampling position:

- The flue should not be so large that the gas velocity is less than 3 m/s.
- Cost and labour of making access holes should be considered. Preference will usually be given to a position in a steel duct rather than a brick flue.
- Accessibility – there must be sufficient room for inserting and withdrawing the sampling probe through the access holes.
- Flue gas temperatures should normally be kept to below 400^{o}C when sampling of soot is required.
- Comfort and convenience of people taking the samples should be considered as it can be very unpleasant to work near the top of a chimney stack. Mistakes and manipulative errors are very easy to make due to working conditions often not being conducive to the maintenance of close attention to details. Some examples of adverse conditions include the ambient temperature may be high, the probe tube is hot to handle, the work space may be cramped and at a considerable height above the ground, the noise may make communication between operators difficult and vibration and movement of the platform may disturb the levelling of the inclined gauge.

viii. Mode of Boiler Operation

When the occasion and period of sampling are being chosen, careful consideration should be given to the exact nature of the ‘average’ emission that is to be measured. When the purpose is to assess the amount of atmospheric pollution caused by the plant, the ‘average’ emission would be required to be a typical value, neither

excessively high nor unduly low as a result of unusual combustion rates, operating conditions, fuel supplies, or of the special inclusion or omission of operations such as soot-blowing. Thus, the reproducibility of the emission includes not only the errors of measurement on one occasion for one sampling period under plant conditions that are regarded as typical, but also the reproducibility of the plant conditions. Practical experience suggests that whilst large water-tube boilers can be and are operated consistently, shell boilers will often be operated so variably from day to day or week to week that the errors of measurements may be small compared with the changes in the level of emission (Hawksley et al., 1977, p 70).

3.3.2. ACHIEVING VALID MEASUREMENTS

Valid measurements can only be achieved in accordance with ISO 9096:2003 when:

a) An adequate quantity of dust is collected during the sampling, which must be a minimum of at least five times the corresponding overall blank value;
b) The gas stream in the duct at the sampling location has a sufficiently steady and identified velocity temperature and pressure, and a sufficiently homogeneous composition;
c) The flow of the gas is parallel to the axis of the nozzle;
d) Sampling is carried out without disturbance of the gas stream, using a sharp-edged nozzle facing into the stream;
e) Isokinetic sampling conditions are maintained throughout the test;
f) Samples are taken at a preselected number of stated positions in the sampling plane to permit obtaining a representative sample for a non-uniform distribution of particulate matter in the duct or stack;
g) The sampling train is designed and operated to avoid condensation and to be leak-free;
h) Calibration criteria are satisfied;
i) Sampling blank and leak-check criteria are met;
j) Dust deposits upstream of the filter are recovered and are taken into account;
k) The sampling and weighing procedures are adapted to the expected dust quantities as specified by the standard.

All the above-mentioned parameters are in control of the sampling specialist, except for the sampling location and plant operating conditions. It is for this reason that the sampling location and plant operating conditions at the time of measurement are said to have the greatest potential influence on the final results reported. This is provided the sampling specialist takes enough care to ensure all the above parameters under his or her control are adhered to.

3.4 MOTION OF PARTICLES IN FLUIDS

Particles contained in a flowing fluid do not move exactly in step with it unless they are so fine as to be virtually indistinguishable from the molecules of the fluid, which for the present application is the case for soot particles (Hawksley et al., 1977, p 91). Thus, although the prediction of the behavior of a suspension of soot in flue gases is relatively straight forward, the problem is much more difficult in systems of dust and grit particles, which owing to their greater inertia in comparison with the fluid, tend to persist in their original directions of motion and do not so readily follow changes in the paths of the fluid streamlines (Hawksley et al., 1977, p 91).

In principle, the path of each can be predicted and the overall behavior of the suspension found by adding the contributions due to particles of various sizes. The concentrations, however, are usually so low that the particles move independently of each other (Hawksley et al., 1977, p 91). The method is first to establish the variations in the velocity of fluid flow from point to point throughout the system under consideration and then to deduce the trajectories of the particles from their equations of motion, the fluid flow being assumed steady and invariable in time (Hawksley et al., 1977, p 91).

The feasibility of the trajectory calculations and the usefulness of the results, however, are limited for a number of reasons according to Hawksley.

- The aerodynamic characteristics of the particles (that is, the mass distribution of stokes' velocities) are neither consistent nor predictable for solids in flue gases – only for pulverized fuel fired installations is the

density and size distribution of dust similar from one plant to another – nor measurable without great difficulty and labour.

- The pattern of the gas flow itself is not known for many important cases; there is very little information on the effect of a simple 90^{o} bend, less on the flow pattern within a cyclone, and practically none at all on the flow into an aspirated sampling nozzle.
- In the case of obstacles, collection by impaction has had to be calculated from the distribution of velocity given by potential flow theory for ideal non-viscous fluids, for the very low Reynolds numbers of viscous flow, the calculations are also limited to the few geometric shapes – spheres, cylinders and discs – for which the fluid flow pattern can be deduced theoretically. Even when both the particle characteristics and velocity pattern are known, there is still the labour of the step-wise calculations; the algebraic expressions are generally too complex for an analytical solution and recourse must be made to numerical methods with the aid of computing machines.
- A further consideration is that in practice, the fluid flow is turbulent, the Reynolds number of flow of flue gases in flue ducting and chimney stacks rarely being less than 250000 (see Reynolds number calculations on pages 53 - 54 for the data set used).
- It is important to note that the non-uniform distribution of solids produced by a bend is corrected by turbulent mixing within a distance of a few pipe diameters. About three to five diameters is usually sufficient, hence the requirement of five hydraulic diameters is given in ISO9096 - see p 31, Table 3.1 minimum requirements.

For several reasons including the ones mentioned above, the sampling location is deemed to be the largest source of error contributing to the overall uncertainty of the final measurement results reported (see chapters 2 sub section 2.2 and 3 sub section 3.2 respectively). It is for this reason that the velocity profiles for the individual test results in both the compliant (Source A) and non-compliant (Source B) sampling campaigns are included.

For the purposes of this study a compliant stack is defined as a stack that complies with all the relevant minimum criteria as set out in ISO 9096:1992 and 2003. A non-

compliant stack is defined as a stack that complies with all the relevant minimum criteria as set out in ISO 9096:1992 and 2003, except for compliance to the sampling location. A compliant sampling location should be located a minimum of five hydraulic diameters downstream from any obstructions, bends etc. and five hydraulic diameters upstream from the stack exit. If this minimum requirement is met, the flow at the sampling plane should be sufficiently stable and uniform to allow for accurate isokinetic sampling to be achieved.

The velocity profile measured at each sampling location should therefore provide a good indication of whether the sampling location is acceptable. If the flow is sufficiently stable and uniform the subsequent statistical analysis should give a normal distribution. Each individual velocity data set was assessed for normality and whether or not the flow inside the enclosed flue gas system was laminar or not.

3.5 RULES FOR NORMALLY DISTRIBUTED DATA

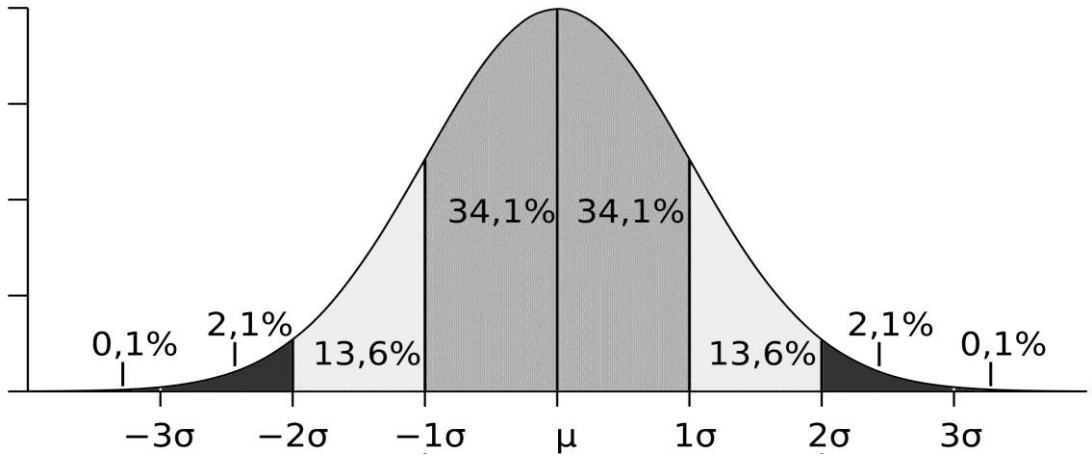

Figure 3.1 Graphical illustration of a normal distribution (Source: Jeremy Kemp, 2009)

The dark grey shaded area in figure 4.1 is less than one standard deviation from the mean. For the normal distribution, this accounts for 68.27% of the set; while two standard deviations from the mean (dark and light grey areas) account for 95.45%; and three standard deviations (dark grey, light grey and black areas) account for 99.73%.

In practice, one often assumes that the data are from an approximately normally distributed population. If that assumption is justified, then about 68% of the values are within 1 standard deviation of the mean, about 95% of the values are within two standard deviations and about 99.7% lie within 3 standard deviations. This is known as the "68-95-99.7 rule", or "the empirical rule". For stack emission monitoring, the nature of factors contributing to the uncertainty is such that it is not justifiable to say the concentration is certain to be in the range 41 to 49 mg/m^3. However, if the uncertainty of 4 mg/m^3 was calculated with a level of confidence of 95%, then it can be assumed that 95 times out of 100 the result would be within those bounds. This enables regulatory bodies to interpret measurements and their uncertainties with respect to limit values and issues regarding demonstration of compliance (Technical Guidance note. M2, Version 3, October 2004). The final reported results must always contain a note on the uncertainty of the values reported together with the level of confidence.

CHAPTER 4: RAW DATA STATISTICAL ANALYSIS

4.1 VALIDATION OF RESULTS

If testing was conducted at an unsuitable location, or was carried out under fluctuating plant operating conditions, the validity of the sample may be questioned and the measurement results uncertain (ISO9096:2003). An assessment of the stability and uniformity of the flow in the flue will determine the suitability/compliance of the sampling location. For this reason the velocity flow profiles for Source A and B have been included (See Figures 4.2 - 4.10).

4.2 COMPLIANT SOURCE (SOURCE A)

4.2.1 MEASURED COMPONENTS

A series of six isokinetic measurements for particulate matter were conducted under normal plant operational conditions at Source A. The flow profiles for each individual

test are included in order to illustrate the potential effects on the stability of flow between a compliant and non-compliant sampling location. From the data obtained, only certain samples were selected for comparison, as these were deemed to represent the most stable similar plant operating conditions. Where sampling was conducted under varying plant operating conditions the results were excluded from the data sets.

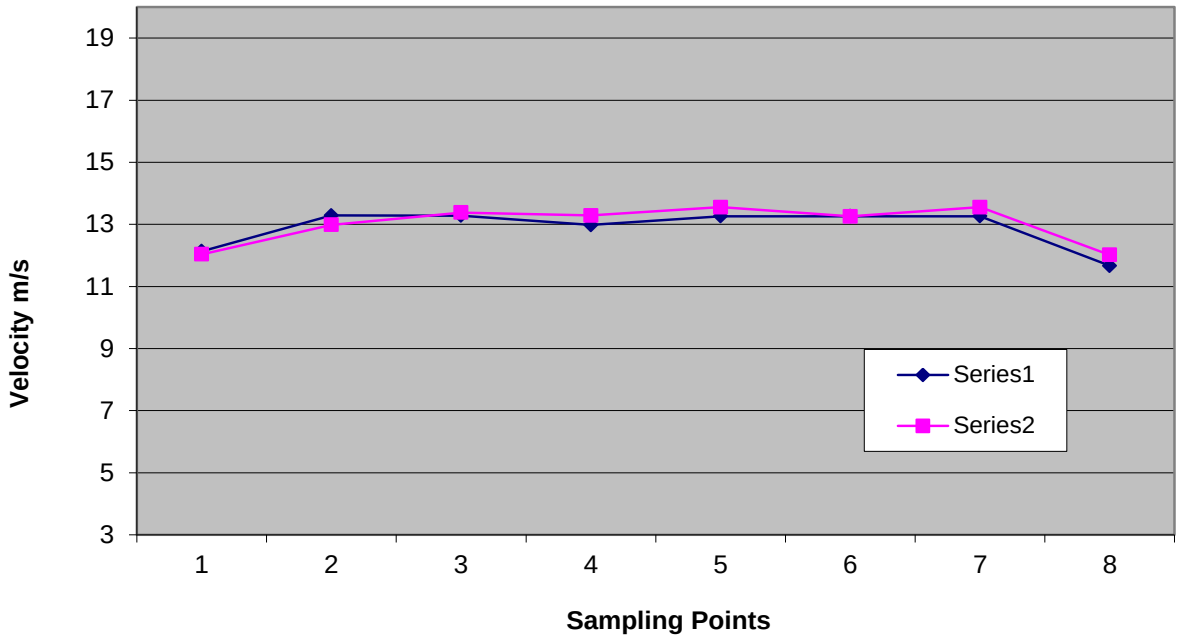

Figure 4.1 Velocity profile for test 1 Source A

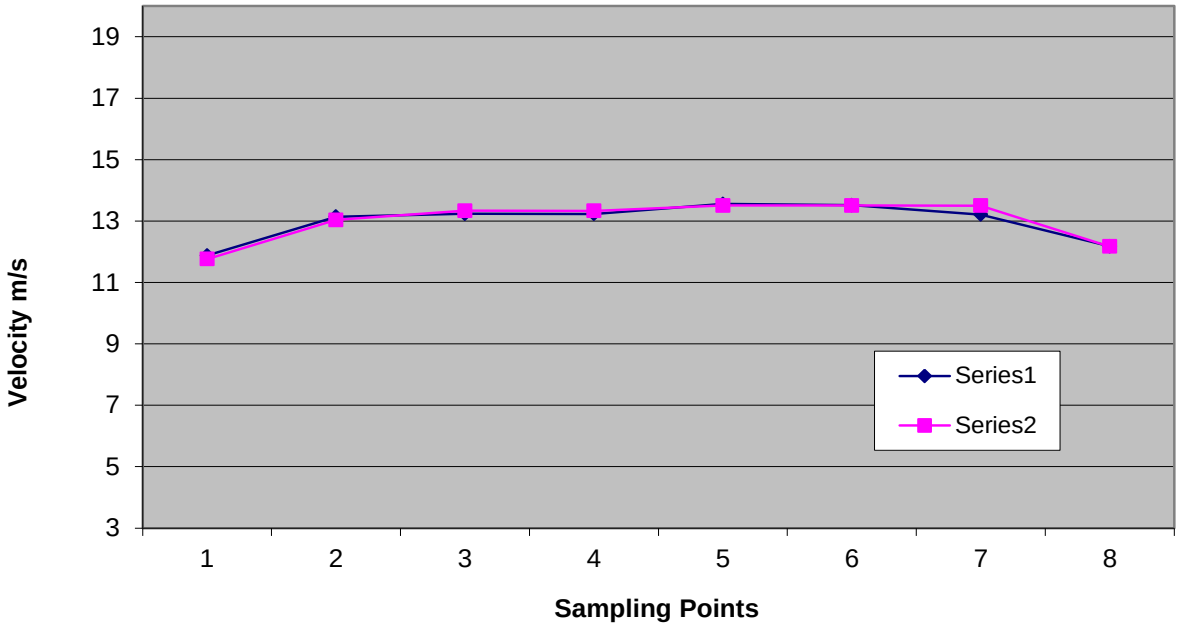

Figure 4.2 Velocity profile for test 2 Source A

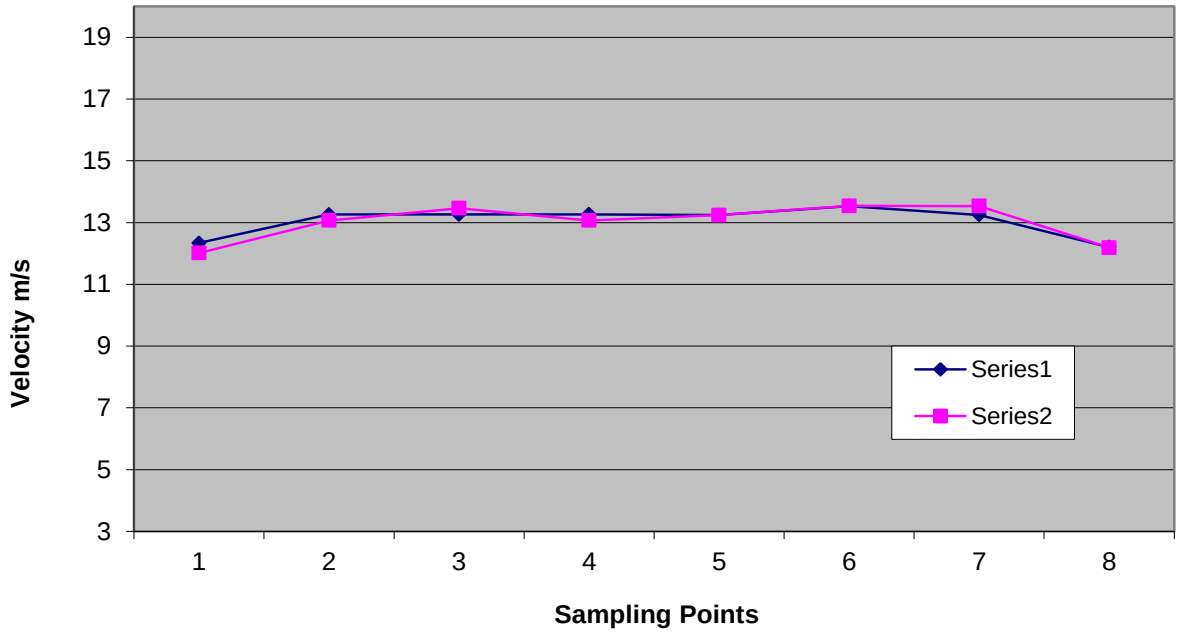

Figure 4.3 Velocity profile for test 3 Source A

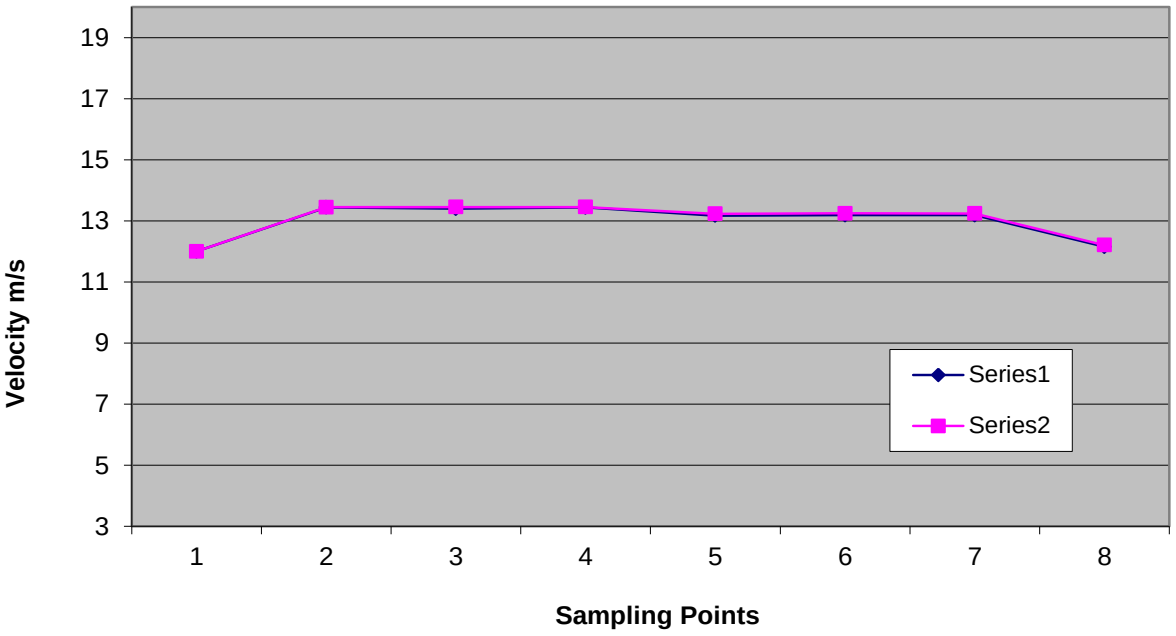

Figure 4.4 Velocity profile for test 4 Source A

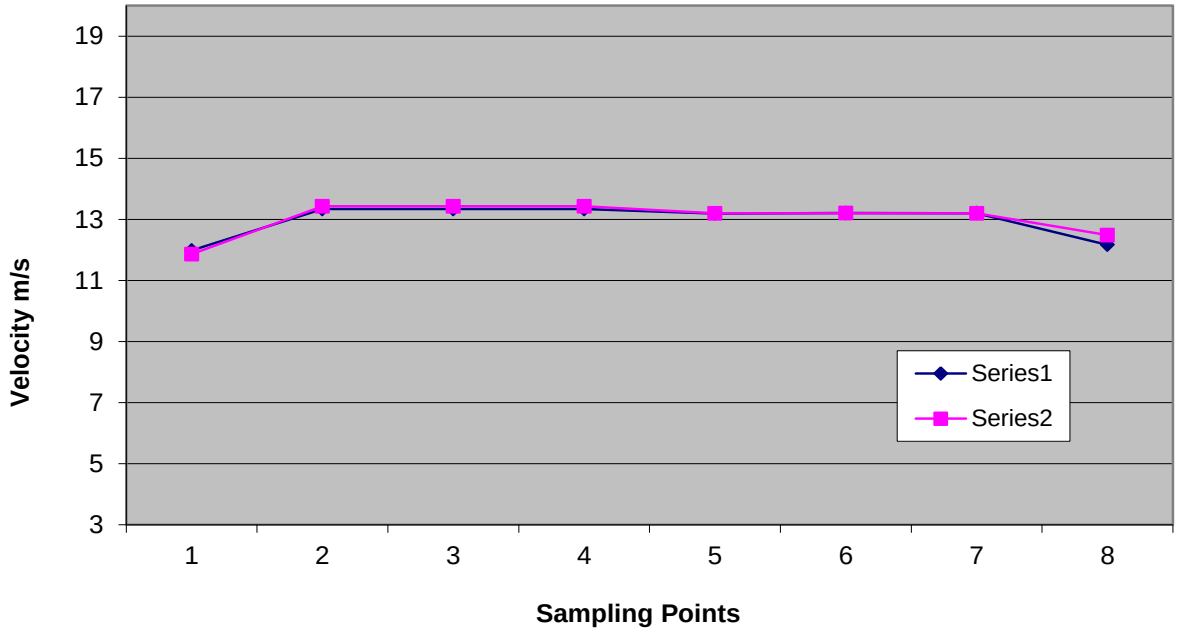

Figure 4.5 Velocity profile for test 5 Source A

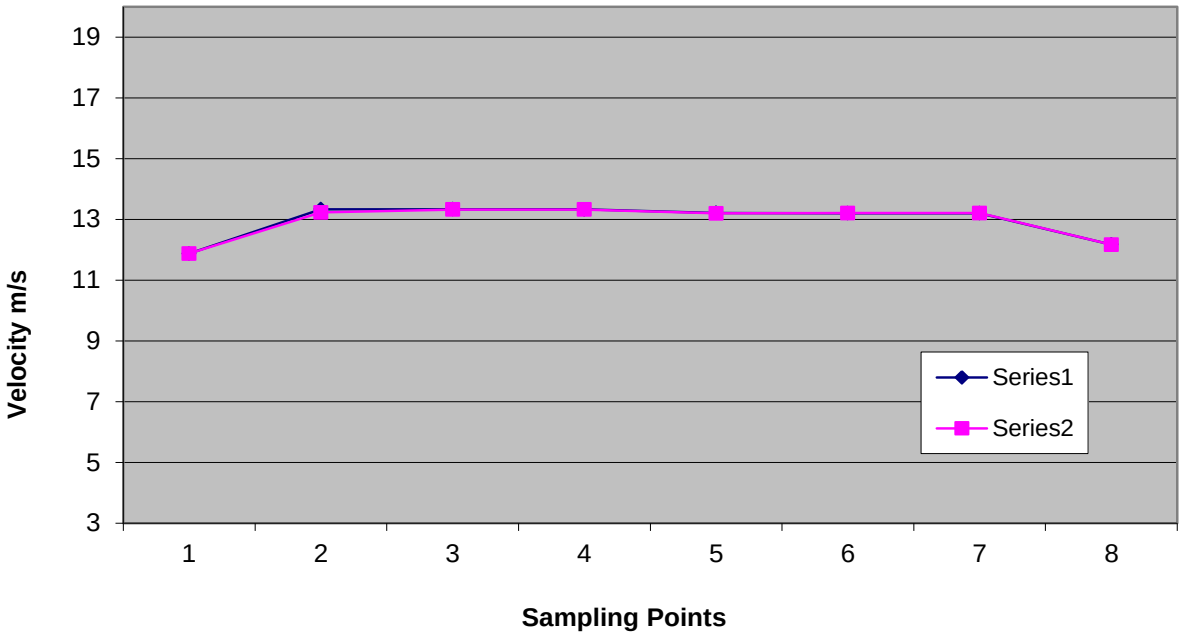

Figure 4.6 Velocity profile for test 6 Source A

From the data presented in figures 4.2 – 4.7, one can deduce that the flow pattern within the flue at this sampling location is stable and uniform, which is consistent with an ISO 9096 compliant sampling location. Stable uniform flow is defined by the standard as per Table 3.1 sample location requirements. If these criteria are met, then the flow is regarded as uniform and stable for the purposes of the method.

ISOKINETIC TEST RESULTS

PLANT COMPLIANT SAMPLING POSITION
DATE 01-Aug-05

DATA NO.	Dust [conc] mg/Nm^3	CO_2	O_2	Static Pressure	Moisture	Gas Temp	Gas Velocity	Gas Density
1	287.65	11.10	8.20	-1.10	2.33	125.45	12.99	0.75
2	293.30	11.10	8.20	-1.11	3.80	125.65	13.03	0.75
3	315.89	11.10	8.20	-1.05	3.77	127.66	13.13	0.74
4	318.30	11.50	8.10	-1.05	2.30	123.96	13.08	0.75
5	396.23	11.50	8.10	-1.05	2.42	124.69	13.28	0.75
6	428.34	11.50	8.10	-0.98	2.19	126.03	13.22	0.75
PARAMETER								
sum	2039.71	67.80	48.90	-6.34	16.81	753.44	78.73	4.49
average	339.95	11.30	8.15	-1.06	2.80	125.57	13.12	0.75
median	317.10	11.30	8.15	-1.05	2.38	125.55	13.11	0.75
variance	2823.22	0.04	0.0025	0.0018	0.49	1.33	0.01	0.000014
SD	53.13	0.20	0.05	0.04	0.70	1.15	0.10	0.0037
confidence (95%)*	130.18	0.49	0.12	0.10	1.71	2.82	0.25	0.01
% Uncert	15.63	1.77	0.61	4.00	24.94	0.92	0.78	0.50
% Uncert (95% CI)*	38.29	4.34	1.50	9.81	61.09	2.25	1.90	1.22

Combined Standard Uncertainty	53.15
Combined Expanded Uncertainty	130.221
Combined Standard Uncertainty % Relative	29.79
Combined Expanded Uncertainty % Relative	72.98

*where CI = 95%, K = 2.45, degrees of freedom = 6

PLANT COMPLIANT SAMPLING POSITION
DATE 04-Aug-05

DATA NO.	Dust [conc] mg/Nm^3	CO_2	O_2	Static Pressure	Moisture	Gas Temp	Gas Velocity	Gas Density
1	159.60	11.50	8.10	-1.20	4.00	123.51	13.19	0.75
2	188.86	11.50	8.10	-1.20	2.73	125.63	13.14	0.75
3	192.32	11.50	8.10	-1.20	4.11	125.45	13.11	0.75
4	218.84	11.40	8.20	-1.07	5.26	122.91	13.12	0.75
5	236.85	11.40	8.20	-1.07	5.08	123.69	13.17	0.75
6	254.29	11.40	8.20	-1.05	4.63	124.00	13.12	0.74
PARAMETER								
sum	1250.76	68.70	48.90	-6.79	25.81	745.19	78.85	4.49
average	208.46	11.45	8.15	-1.13	4.30	124.20	13.14	0.75
median	205.58	11.45	8.15	-1.14	4.37	123.85	13.13	0.75
variance	1007.68	0.0025	0.0025	0.0047	0.70	1.01	0.0008	0.000014
SD	31.74	0.05	0.05	0.07	0.84	1.00	0.03	0.0037
confidence (95%)	77.77	0.12	0.12	0.17	2.06	2.46	0.07	0.01
% Uncert	15.23	0.44	0.61	6.07	19.52	0.81	0.22	0.50
% Uncert (95% CI)	37.31	1.07	1.50	14.86	47.82	1.98	0.54	1.22

Combined Standard Uncertainty	31.77
Combined Expanded Uncertainty	77.8393
Combined Standard Uncertainty % Relative	25.52
Combined Expanded Uncertainty % Relative	62.52

*where CI = 95%, K = 2.45, degrees of freedom = 6

Table 4.1 MEASURED PARAMETERS AND THEIR ESTIMATED UNCERTAINTY

4.2.2 COMBINED UNCERTAINTY FOR MEASURED VARIABLES

The measured parameters for all of the six individual tests conducted on Source A are illustrated in Table 4.1. An estimate of uncertainty was attempted but the results were not conclusive as not enough data were obtained to enable any valid statistical

inferences to be made. The estimated combined expanded uncertainty at a 95% confidence interval was 130 and 77 respectively. This indicates that there is a high variability in the data set obtained. In addition to the high variability obtained the data sets are very limited and ultimately too small to place high degree of confidence in the uncertainties calculated.

4.2.3 STATISTICAL TOOLS UTILIZED

The following statistical tools were utilized in the calculations from the data.
The data were deemed to be of a normal distribution. Due to a lack of sufficient data, this is assumed to be the case and could not be statistically verified. All the off-gas measured parameters have been incorporated into table 4.1 together with the measured result. For each set of data, the following results were calculated in order to derive the final combined expanded uncertainty for each parameter:

- Step 1: Tabulate all the raw data results
- Step 2: Calculate the sum of all the results
- Step 3: Calculate the average for the data set from the sum of the results
- Step 4: Calculate the median for the data set
- Step 5: Calculate the variance

  $(s^2) = \Sigma [(x_i - \overline{x})^2]/n - 1.$

  Where:

  - s^2 = Variance
  - Σ = Summation, which means the sum of every term in the equation after the summation sign.
  - x_i = Sample observation. This represents every term in the set.
  - $\overline{x}$ = The mean. This represents the average of all the numbers in the set.
  - n = The sample size. You can think of this as the number of terms in the set.
- Step 6: Calculate the standard deviation

  $$s = \sqrt{\frac{\sum(x - \overline{x})^2}{N - 1}}$$

  Where:

  - S = standard deviation
  - x = each value in the sample
  - $\overline{x}$ = The mean of the values

- N = the number of values (the sample size)

- Step 7: Calculate uncertainty at 95% confidence interval
  - Utilise the student's t-distribution table to determine the coverage K factor from the degrees of freedom for the data set for the equivalent 95% confidence interval.
- Step 8: Calculate combined standard uncertainty

$$CU = \sqrt{u_1^2 + u_2^2 + \cdots + u_n^2}$$

or

$$CU = (u_1^2 + u_2^2 + \cdots + u_n^2)^{\frac{1}{2}}$$

Where:

- CU = combined uncertainty
- U = uncertainty of individual component

4.3 NON-COMPLIANT SOURCE (SOURCE B)

4.3.1 MEASURED COMPONENTS

A series of three isokinetic measurements for particulate matter were conducted under normal plant operational conditions at Source B. The flow profiles for each individual test are included in order to illustrate the potential effects on the stability of flow between a compliant and non-compliant sampling location.

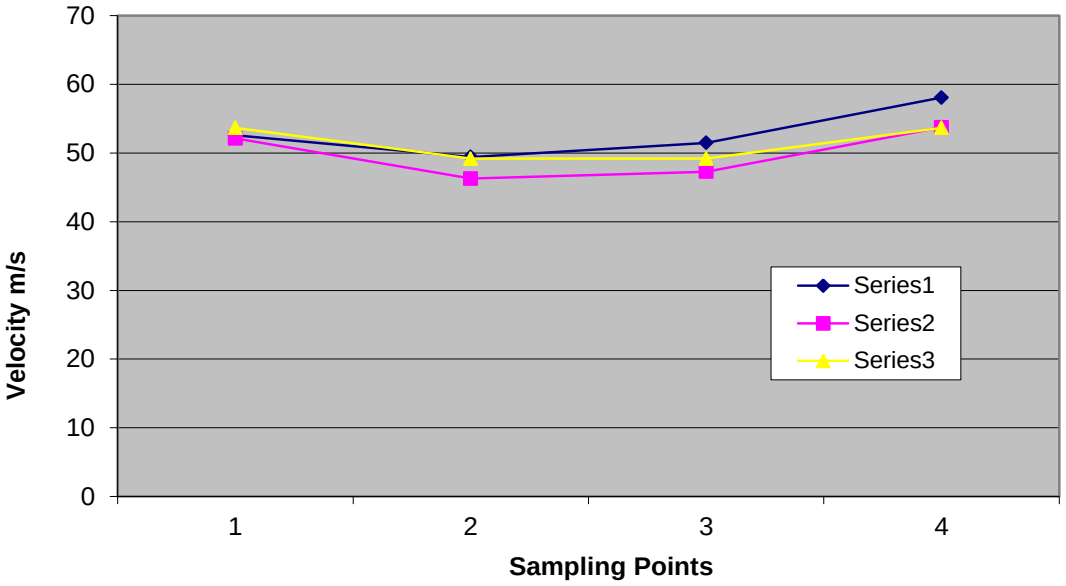

Figure 4.8 Velocity profile for test 1 Source B

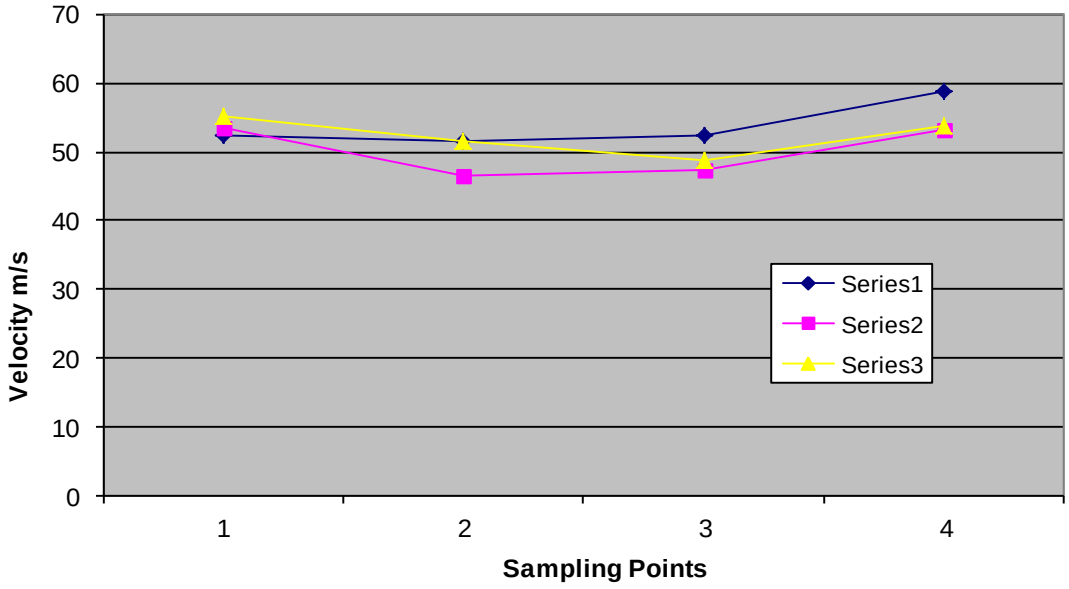

Figure 4.9 Velocity profile for test 2 Source B

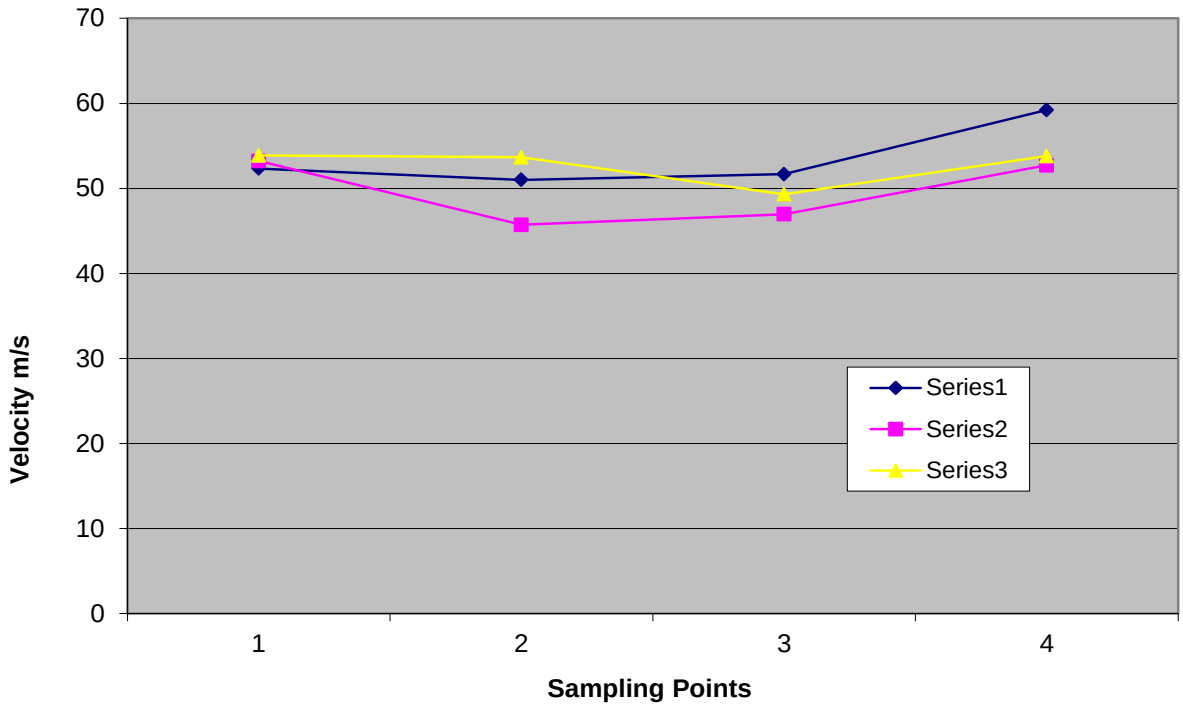

Figure 4.10 Velocity profile for test 3 Source B

From the data presented in figures4.8 – 4.10 one can deduce that the flow pattern within the flue at this sampling location is unstable and irregular which is consistent with an ISO 9096 non-compliant sampling location.

4.3.2 COMBINED UNCERTAINTY FOR MEASURED VARIABLES

The measured parameters for all of the three individual tests conducted on Source B are illustrated in Table 4.2. An estimate of the overall uncertainty was attempted but the results were not conclusive as not enough data were obtained to enable any valid statistical inferences to be made.

If one compares the calculated overall uncertainty for Tables 4.1 and 4.2, one would notice that the non-compliant data set returns a similar overall uncertainty (62.52-72.98) when compared to the compliant stack (62.69%). The overall uncertainty is also much higher than anticipated; this once again is mainly attributed to the small data sets utilized and the number of external variables that cannot be accounted for (i.e. certain process operating conditions, changes in environmental conditions etc.)

This small study has confirmed findings of a comparable but larger project which came to similar conclusions. The Dutch study mentioned in ISO 9096:2003 collected much larger data sets than the one used in this study, yet had very high levels of uncertainty when trying to calculate an overall uncertainty for the entire data set. Prior to the Dutch field-based study being undertaken (ISO9096:2003, p38), a sensitivity analysis was conducted of the uncertainty of the entire document. "This led to the conclusion that the determination of the waste gas velocity (i.e. mispositioning of the Pitot tube) had contributed most to the total measuring uncertainty"(ISO9096:2003, p38). In turn, a non-complying sampling location can also have a significant effect on the velocity profile (See figures 4.2 – 4.10) and ultimately affect the total measurement uncertainty in the same way as a mispositioned Pitot tube.

ISOKINETIC TEST RESULTS

PLANT NON-COMPLIANT SAMPLING POSITION
DATE 10-Nov-05

DATA NO.	Dust [conc] mg/Nm^3	CO_2	O_2	Static Pressure	Moisture	Gas Temp	Gas Velocity	Gas Density
1	1694.52	23.00	11.00	-1.00	9.68	93.17	52.44	0.83
2	1813.39	22.00	11.00	-1.00	12.89	95.00	53.50	0.82
3	2051.77	22.00	12.00	-1.08	12.72	95.75	53.39	0.82
PARAMETER								
sum	5559.68	67.00	34.00	-3.08	35.29	283.92	159.33	2.47
average	1853.23	22.33	11.33	-1.03	11.76	94.64	53.11	0.82
median	1813.39	22.00	11.00	-1.00	12.72	95.00	53.39	0.82
variance	22064.74	0.22	0.2222	0.0014	2.17	1.17	0.23	0.000022
SD	181.93	0.58	0.58	0.05	1.81	1.33	0.58	0.01
confidence (95%)*	578.53	1.84	1.84	0.15	5.74	4.22	1.85	0.02
SD % Relative	9.82	2.59	5.09	4.50	15.35	1.40	1.10	0.70
% Uncert (95% CI)*	31.22	8.22	16.20	14.31	48.83	4.46	3.49	2.23

Combined Standard Uncertainty	181.94
Combined Expanded Uncertainty	578.5778
Combined Standard Uncertainty % Relative	19.71
Combined Expanded Uncertainty % Relative	62.69

*where CI = 95%, K = 3.18, degrees of freedom = 3

Table 4.2 MEASURED PARAMETERS AND THEIR ESTIMATED UNCERTAINTY

4.4 CALCULATING LAMINAR FLOW

The equation (2) was utilized to calculate whether the flow in a compliant (Scenario A) stack was laminar. The calculation of the Reynolds number for the flow profile in the waste gas was attempted in order to answer the following assumption:

If laminar flow could be ascertained, then can sample location compliance be proven?

REYNOLDS NUMBER RESULTS (2)

$$R = \frac{\rho V D}{\mu}$$

Where: ρ = density (kg/m^3)
V = Fluid velocity (m/s)
D = Diameter (m)
μ = Dynamic fluid viscosity (kg/m-s)

PLANT: COMPLIANT SAMPLING POSITION
DATE: 01-Aug-05

Parameter	Measured	Calculated		
N_2*	%	Kg/Nm^3	80.55	1.01
CO_2	%	Kg/Nm^3	11.3	0.22
O_2	%	Kg/Nm^3	8.15	0.12
Static Pressure	mb	Pa	-1.06	-106
H_2O	%	Kg/Nm^3	2.8	0.02
Gas Temperature	oC	K	125.5	398.65
Gas velocity	m/s	m/s	13.12	13.12
Gas density		Kg/m^3	N/A	0.75
Stack Diameter	m	m	16.62	16.62
Dynamic Viscosity		Kg/m-s		$2.139x10^{-5}$

Reynolds number = $\underline{7.65*10^6}$

- Plate flow is therefore fully turbulent at a distance D from the leading edge
- Pipe flow is fully turbulent in a pipe of diameter D

* Calculated by difference

PLANT: NON-COMPLIANT SAMPLING POSITION

DATE: 10-Nov-05

Parameter	Measured	Calculated		
N_2*	%	Kg/Nm^3	66.67	0.83
CO_2	%	Kg/Nm^3	22.33	0.44
O_2	%	Kg/Nm^3	11.00	0.16
Static Pressure	mb	Pa	-1.03	-103
H_2O	%	Kg/Nm^3	11.76	0.09
Gas Temperature	oC	K	94.64	367.79
Gas velocity	m/s	m/s	53.11	53.11
Gas density		Kg/m^3	N/A	0.75
Stack Diameter	m	M	2.41	2.41
Dynamic Viscosity		Kg/m-s		$2.733x10^{-5}$

Reynolds number = $\underline{3.84*10^6}$

- Plate flow is therefore fully turbulent at a distance D from the leading edge
- Pipe flow is fully turbulent in a pipe of diameter D

* Calculated by difference

As can be seen from the results obtained above for both the compliant and non-compliant sampling locations, the Reynolds number provides little information as the fluid flow is high, and typically fluid flow is turbulent in flue ducting and chimney stacks (Hawksley et al., 1977).

4.5 DISCUSSION

The statistical analysis of the data reveals much about the data. It highlights the fact that no conclusive opinions can be made about the data sets utilized.

After applying the statistical methodology to the data sets, it was concluded that the data sets were far too small. Ideally 50 – 100 or more samples need to be included in

each of the data sets (GUM 1995). Unfortunately, obtaining a large enough data set has not been possible due to budget constraints and the cost and logistics of conducting the sampling. The standard deviation for the test results is not consistent over the range of results and this is attributed to the small data set.

Due to the nature of field sampling, all variables cannot be controlled. The samples are all taken at different times at supposedly the same plant operating conditions. Although this is the case for each individual source variation in the results still occurs as a result of a large number of input variables involved i.e. sampling procedure, process operation, plant and prevailing environmental conditions all of which have an influence on the repeatability and reproducibility of the results.

The influence of turbulent flow is said to also have a large negative effect on the overall result. Attempts to calculate Reynolds numbers (see equation 2) for the various flow profiles also revealed no conclusive answers. The compliant as well as the non-compliant sampling positions both showed turbulent flow according to the Reynolds numbers calculated. ISO 9096:1992 and 2003 does not require laminar flow but states that the flow in the duct must be as stable and uniform as possible. To achieve laminar flow, one needs to have very low flow rates, as the flow rates of a typical enclosed flue gas stream is high (for this study the velocity range was between 11.5 – 50m/s), ranging between 5 – 30 m/s - true laminar flow is almost impossible. It is for this reason that the application of the Reynolds number did not confirm compliance or non-compliance of the sampling position. The survey and statistical analysis is not, however, all in vain as it shows that the uncertainty cannot be estimated quantitatively, as attempted with the statistical analyses due to the data set being too small.

An alternative method / tool to utilizing statistical techniques is to use qualitative estimates of uncertainty based on experience, reasonable estimates of errors and uncertainties and adherence to the minimum requirements of the ISO9096:1992 and 2003 standards which has been developed by the author. The result of this approach has been the development of a sampling suitability matrix. This matrix consists of a table with all the minimum requirements, as set out in ISO9096:2003 (see p 31). From the Table, the accuracy and minimum requirements for all the apparatus and sampling conditions are given.

Utilizing this method, once the sampling survey has been completed the sampling specialist will check each of the components for compliance. A rating scale has been devised according to the influence each component is estimated to have on the final results. These values have largely been derived from experience in the field and the ability for the sampling specialist to control certain variables (systematic errors).

CHAPTER 5: DEVELOPMENT OF A SAMPLE SUITABILITY MATRIX

5.1 PRINCIPLES AND PHILOSOPHY BEHIND DEVELOPMENT OF THE RATING CRITERIA

A rating scale has been devised according to the influence each component is estimated to have on the final results. These values have largely been derived from experience in the field and the ability for the test engineer to control certain variables.

All the measurement variables have been tabulated and categorized (see Table 5.2). The measurement variables have been placed into three categories including sampling location, equipment used for dust collection, and equipment for flue gas characteristics (ISO 9096:2003, see p 31). Each variable has been given a rating out of ten, the higher the number out of ten, the greater the influence of the variable on the uncertainty of the final sampling results. The rating is subjective; the principle behind the rating of each variable is the ability of the test engineer to control that specific variable. The less control the test engineer has over the variable, the higher the rating.

From Table 5.1, the accuracy for all the components of the measurement variables is given. Once the sampling survey has been conducted, the sampling specialist will check each of the components for compliance to the minimum requirements (ISO 9096:2003). The highest ratings have been given to those variables that are as a result of plant restrictions and deemed to be totally out of control of the sampling specialist. The ratings are based on a sliding scale with a score of ten having been estimated to have the most impact on the final measurement uncertainty and a rating of one having the lowest impact on the final measurement result. A zero value indicates that the plant is not in compliance for that parameter and therefore the overall points scored will be lowered according to the weighting assigned to each components' estimated impact on the final result. Once all the components or variables have been checked for compliance, the sampling specialist will calculate each specific component rating. The sampling specialist will input all the results and ratings into the sampling suitability table that will estimate the quality of the final measurement result as excellent, fair or poor (see Tables 5.1, 5.2 and 5.3).

5.2 SAMPLING SUITABILITY MATRIX

Table 5.1 Sampling Suitability Matrix (Master Template)

Summary of requirements - Apparatus and sampling conditions

SAMPLING LOCATION	Approx. Value	Measured Value	compliance y/n	Rating	
Flow angle	$<15^{o}$			10	P
Pressure difference (pitot tube)	> 5 Pa			10	P
Ratio of max gas velocity to min gas velocity	3:1			10	P
Negative flow	None			10	P
Straight length before the sampling plane	> 5 hydraulic diameters			9	P
Straight length after the sampling plane	> 2 hydraulic diameters			9	P
straight length before emission point	> 5 hydraulic diameters			9	P
Number of sampling points	dependant on duct size			9	P
EQUIPMENT FOR DUST COLLECTION					
Alignment of the nozzle	10%			8	FS
Isokinetic Criteria	+15% and - 5 %			8	FS
Leak test	<2%			8	FS
Condenser, drying tower: residual gas moisture	$< 10\ g/m^3$			7	FS
Gas meter volume measurement uncertainty	2%			7	FS
Absolute pressure measurement uncertainty	1%			7	FS
Absolute temperature measurement uncertainty	1%			7	FS
filter efficiency (test aerosol 0,3um)	> 99.5 %			6	EQ
Filter material (adsorption of components)	No reaction or adsorption			6	EQ
Nozzle straight length before the first bend	> 30 mm			5	EQ /P
Nozzle tip: distance to obstacles	> 50 mm			5	EQ /P
Nozzle: Length with constant internal diameter	>10mm			4	EQ
Nozzle: variation in diameter angle	$< 30^{o}$			4	EQ
Nozzle Internal diameter	>4mm			4	EQ
Nozzle area: measurement uncertainty	10%			4	EQ
Elbow: Radius of the bend	$> 1{,}5d$			4	EQ
Balance resolution (mg)	0.01mg to 0.1mg			3	L
weighing uncertainties	<5% of the LV for process			3	L
Thermal stability (filter)	>8h			3	L
Overall Blank Value	$<10\%$ LV or $2\ mg/m^3$			3	L
Sampling time measurement uncertainty	5secs			2	FS
linear measurement uncertainty	1% duct .2mm / 5% Nozzle			2	FS
EQUIPMENT FOR FLUE GAS CHARACTERISTICS					
Absolute temperature	1%			1	C
Flue gas density	$0{,}05\ kg/m^3$			1	C
Total possible Score				188	
Validity of Results obtained					%
Excellent (Fully compliant)				188	1.00
Fair (mostly compliant)				150	0.80
Poor				60	0.32

Key:
P: Plant Restrictions
FS: Field Sampling Restrictions
EQ: Equipment Restrictions
L: Laboratory Restrictions
C: Calculated / Measured in the Field

5.3 APPLICATION OF MATRIX TO THE DATA SETS

The sampling suitability matrix master template was applied to the surveys utilized in this project for the purpose of comparing a fully compliant (Source A, table 5.2) and non-compliant (Source B, table 5.3) survey and how the sampling suitability matrix rates the different surveys and if the results correlate.

Summary of requirements - Apparatus and sampling conditions

SAMPLING LOCATION	Approx. Value	Measured Value	compliance y/n	Rating	
Flow angle	<15^{o}		y	10	P
Pressure difference (pitot tube)	> 5 Pa		y	10	P
Ratio of max gas velocity to min gas velocity	3:1		y	10	P
Negative flow	None		y	10	P
Straight length before the sampling plane	> 5 hydraulic diameters		y	9	P
Straight length after the sampling plane	> 2 hydraulic diameters		y	9	P
straight length before emission point	> 5 hydraulic diameters		y	9	P
Number of sampling points	dependant on duct size		y	9	P
EQUIPMENT FOR DUST COLLECTION					
Alignment of the nozzle	10%		y	8	FS
Isokinetic Criteria	+15% and - 5 %		y	8	FS
Leak test	<2%		y	8	FS
Condenser, drying tower: residual gas moisture	< 10 g/m^{3}		y	7	FS
Gas meter volume measurement uncertainty	2%		y	7	FS
Absolute pressure measurement uncertainty	1%		y	7	FS
Absolute temperature measurement uncertainty	1%		y	7	FS
filter efficiency (test aerosol 0,3um)	> 99.5 %		y	6	EQ
Filter material (adsorption of components)	No reaction or adsorption		y	6	EQ
Nozzle straight length before the first bend	> 30 mm		y	5	EQ /P
Nozzle tip: distance to obstacles	> 50 mm		y	5	EQ /P
Nozzle: Length with constant internal diameter	>10mm		y	4	EQ
Nozzle: variation in diameter angle	< 30^{o}		y	4	EQ
Nozzle Internal diameter	>4mm		y	4	EQ
Nozzle area: measurement uncertainty	10%		y	4	EQ
Elbow: Radius of the bend	> 1,5 *d*		y	4	EQ
Balance resolution (mg)	0.01mg to 0.1mg		y	3	L
weighing uncertainties	<5% of the LV for process		y	3	L
Thermal stability (filter)	>8h		y	3	L
Overall Blank Value	<10% LV or 2 mg/m^{3}		y	3	L
Sampling time measurement uncertainty	5secs		y	2	FS
linear measurement uncertainty	1% duct .2mm / 5% Nozzle		y	2	FS
EQUIPMENT FOR FLUE GAS CHARACTERISTICS					
Absolute temperature	1%		y	1	C
Flue gas density	0,05 kg/m^{3}		y	1	C
Total possible Score				188	
Validity of Results obtained					%
Excellent (Fully compliant)				188	1.00
Fair (mostly compliant)				150	0.80
Poor				60	0.32

Table 5.2 Sampling Suitability Matrix for Source A

Summary of requirements - Apparatus and sampling conditions

SAMPLING LOCATION	Approx. Value	Measured Value	compliance y/n	Rating	
Flow angle	<15^{o}		n	0	P
Pressure difference (pitot tube)	> 5 Pa		y	10	P
Ratio of max gas velocity to min gas velocity	3:1		n	0	P
Negative flow	None		n	0	P
Straight length before the sampling plane	> 5 hydraulic diameters		n	0	P
Straight length after the sampling plane	> 2 hydraulic diameters		n	0	P
straight length before emission point	> 5 hydraulic diameters		n	0	P
Number of sampling points	dependant on duct size		n	0	P
EQUIPMENT FOR DUST COLLECTION					
Alignment of the nozzle	10%		y	8	FS
Isokinetic Criteria	+15% and - 5 %		y	8	FS
Leak test	<2%		y	8	FS
Condenser, drying tower: residual gas moisture	< 10 g/m^{3}		y	7	FS
Gas meter volume measurement uncertainty	2%		y	7	FS
Absolute pressure measurement uncertainty	1%		y	7	FS
Absolute temperature measurement uncertainty	1%		y	7	FS
filter efficiency (test aerosol 0,3um)	> 99.5 %		y	6	EQ
Filter material (adsorption of components)	No reaction or adsorption		y	6	EQ
Nozzle straight length before the first bend	> 30 mm		y	5	EQ /P
Nozzle tip: distance to obstacles	> 50 mm		y	5	EQ /P
Nozzle: Length with constant internal diameter	>10mm		y	4	EQ
Nozzle: variation in diameter angle	< 30^{o}		y	4	EQ
Nozzle Internal diameter	>4mm		y	4	EQ
Nozzle area: measurement uncertainty	10%		y	4	EQ
Elbow: Radius of the bend	> 1,5 *d*		y	4	EQ
Balance resolution (mg)	0.01mg to 0.1mg		y	3	L
weighing uncertainties	<5% of the LV for process		y	3	L
Thermal stability (filter)	>8h		n	0	L
Overall Blank Value	<10% LV or 2 mg/m^{3}		y	3	L
Sampling time measurement uncertainty	5secs		y	2	FS
linear measurement uncertainty	1% duct .2mm / 5% Nozzle		n	0	FS
EQUIPMENT FOR FLUE GAS CHARACTERISTICS					
Absolute temperature	1%		y	1	C
Flue gas density	0,05 kg/m^{3}		y	1	C
Total possible Score				117	
Validity of Results obtained					%
Excellent (Fully compliant)				188	1.00
Fair (mostly compliant)				150	0.80
Poor				60	0.32

Table 5.3 Sampling Suitability Matrix for Source B

5.4 DISCUSSION

From the sampling suitability matrix table, one can see that the restrictions of the plant as well as field sampling restrictions, time constraints, plant availability, extreme operating conditions, sampling location restrictions and access to the sampling position all have the biggest impact on the final data quality, and therefore have the highest rating (the more requirements in terms of the sampling location and plant restrictions that do not comply, the greater the impact on the results). Equipment restrictions such as limits of detection, calibration and verification of sampling train components, and resolution of sampling train components utilized, may have a significant impact on the results; these variables thus received a moderate rating in terms of impacting the final data quality. The laboratory analyses and calculated values have the least impact on the final results as these are the variables that can be the most controlled by the sampling specialist and laboratory personnel.

The application of the sampling suitability matrix to each data set seems to correlate well when applied to both surveys (Source A and Source B) utilized in this project. The sampling suitability matrix confirmed that the compliant plant (Source A) should generate good reliable data while the non-compliant plant (Source B) has agreed with the results of the sampling suitability matrix in that the results may not be as reliable as the fully compliant plant that was surveyed.

The potential importance of applying the sampling suitability matrix table to post survey results cannot be underestimated. The table's inclusion in the final emissions report will go a long way to highlighting specific problem areas with regards the measurements. The requirement of completing this suitability table will provide a tool for the sampling experts to identify areas of improvement that need to be made to sampling conditions or equipment. It will also go a long way to highlighting the need for identifying suitable sampling locations, stable operating conditions etc. to be provided for by the plant personnel.

CHAPTER 6: SUMMARY AND CONCLUSIONS

When conducting sampling surveys to obtain source emissions data, it has been suggested that the greatest components of error are those that are out of control of the sampling specialist (Random Error); plant operating conditions, environmental conditions, and the non-compliance of the sampling location to the minimum requirements as set out in ISO 9096:1992 and 2003 etc.

The subsequent comparison and analyses of the data between the compliant and non-compliant sampling scenarios has confirmed these suspicions. Once these findings had been established, it was endeavored to find ways through statistical treatment of the data to estimate the uncertainty of the measurements when faced with a non-compliant sampling position.

Determining the measurement uncertainty quantitatively from the analysis of the data in this project was not feasible. The reason for this is that the data sets used in the statistical analysis were too small to derive any conclusions from the results. Due to the labour intensive, time consuming nature and budgetary constraints involved in trying to obtain enough quality data, an alternative qualitative approach was deemed more suitable for the purposes of this study, in order to estimate the uncertainty or overall quality of the final emission data reported. The results of this approach include the development of the sampling suitability matrix which was developed through careful analyses of the minimum requirements as set out in ISO 9096:1992 and 2003 and vast sampling experience. Values have been assigned to all the components and variables that have a significant impact on the quality of the data as set out in ISO9096:1992 and 2003.

The end result is a sampling suitability matrix table that allows the sampling specialist to analyse each component of the sampling survey and assess whether adherence to the minimum requirements have been met. In instances where the minimum requirements for a specific component have not been met, a specific rating has been given to that component which corresponds to the specific impact of its non-compliance to the final emission data reported.

It should be noted that the ratings used are subjective. However the matrix can give a good indication of the quality of the data reported, in the absence of statistically validated data. This is done through careful consideration of the significance and impact that each non-compliance has on the end result.

In conclusion, the sampling suitability matrix would prove to be an invaluable tool in assessing final emissions figures that are reported for sampling campaigns in the future. Even though the original goal of the project was not achieved in terms of quantifying the uncertainty of emissions data, the sampling suitability matrix will be able to give more insight to the client as well as sampling experts in the field on how to interpret the emissions figures reported, and on how reliable the data are. This information will go a long way in helping the decision making process with regards to ensuring environmental compliance. It will give insight into whether enough good quality data have been provided, or whether the results are questionable, resulting in the need for addressing changes to the prevailing sampling conditions, sampling techniques utilized or whether an alternative sampling approach is needed in order to obtain good quality data. Further study into the quantification and estimation of source emission uncertainty will need to be done with larger data sets to enable better interpretation of the results and to allow for a meaningful statistical analysis to be performed.

As mentioned in the introduction, the current trend by industry is to save costs by doing little to comply with the relevant environmental standards. This study has shown this behavior to be short sighted and it may result in much larger costs in the long run and non-compliant permit conditions prevailing as a result of poor data quality.

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