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SAMPLE CONDITIONING ISSUES EMISSIONS MONITORING FROM COMBUSTION PROCESSES

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ABSTRACT

Preventing condensation within gas samples is important if accurate measurement of a soluble component is required - principally nitrogen dioxide within combustion products. Maintaining gas samples above the water or acid dew point is normally achieved by heating the sample transfer lines and gas analyser modules. This paper presents simple methods for the dew point calculation of fossil fuel combustion products and explores the influence of fuel type, air:fuel ratio, combustor pressure and water injection on the dew point, and hence the sample conditioning requirements for particular processes. Sample dilution, low pressure sampling and water removal options are considered as alternatives to heating the sample stream.

The importance of nitrogen dioxide as a source pollutant is also discussed, along with the stringent measures needed to obtain an accurate partition of NO_x - into the monoxide and dioxide - within the sample and how these may conflict with the need to prevent condensation.

1. Background

Obtaining a representative stack gas sample and then ensuring that the components of interest do not undergo chemical or physical change within the sampling train are, self-evidently, crucial in obtaining a 'good' analysis. However, relatively little effort or expenditure is invested in the sampling system when compared with the cost of continuous emissions monitoring equipment. This situation has improved somewhat in recent years, largely as a result of problems in the field which have severe consequences for both end users and suppliers. There are now texts available which provide general coverage of this subject [1] and a description of the increasingly specific requirements of national standards, e.g., U.S. EPA Methods [2].

2. Introduction

It is the intention, in this paper, to draw together published data relating to the sampling and analysis of the 'soluble' components within combustion products which, in turn, is largely a question of preventing condensation within the sample train. The aims are to present information useful in the design of gas sampling systems and to promote a wider understanding of the subject. The emphasis is placed on nitrogen dioxide (NO_2) which is usually assumed to represent a small fraction of the total nitrogen oxides ($NO + NO_2$) but which can, in certain circumstances, predominate. The term 'nitrogen oxides', or 'NO_x', does not include nitrous oxide (N_2O) - a green-house gas found in trace quantities in combustion products and which can be an important intermediate in NO_x formation [3].

Emphasis is given to extractive stack gas sampling, whilst recognising that in-situ cross-duct 'averaging' devices are available [4]. The more stringent demands of 'in-flame' sampling are touched on briefly.

3. Soluble components within combustion products

A gas phase component is considered to be 'insoluble' if it's composition remains substantially unchanged when the sample is passed through an impinger (i.e., bubbled through liquid water). This is true of the components measured routinely to gauge combustion performance: O_2, CO_2, CO and, less frequently, methane and hydrogen. In this case, the water vapour in the sample is generally removed using a condensation trap (knock-out pot) which may incorporate a Peltier cooler (resulting in localised condensation at a surface). The actual sampling conditions are therefore less arduous than an impinger which provides intimate contact between the vapour and liquid phases. Special precautions regarding sample transfer lines are not required; nylon lines are often used and are perfectly acceptable.

The converse is true for a 'soluble' component, mainly the oxides of sulphur and nitrogen, although trace volatile organics can also be lost if water vapour in the sample is allowed to condense [1]. In this case, the gas is generally transported by heated, inert (PTFE) lines. The sample must be maintained above the dew point in order to prevent free water from forming and the subsequent loss of the component by absorption. The dew point is the temperature at, and below which, condensation takes place. Throughout this paper, where the dew point is calculated, a margin of 10 deg.C should be added to the result when considering practical system design.

The dew point can be reduced by sample dilution and the lowering of the sample pressure. These aspects are discussed below. Removal of water from the sample stream by permeation drying is another option. The sample is passed across a surface with a chemical affinity for water. The other side of the membrane is purged with dry air and so one has a selective, non-porous, membrane for water vapour removal. Since the membrane material cannot withstand high temperatures, the dew point must first be reduced to circa 100°C prior to drying, making the system most suitable for sulphur free fuel combustion products. This method is also unsuitable if accurate trace organics measurements are required.

3.1 Nitrogen based compounds

NO_x is formed mainly by the oxidation of fuel-bound nitrogen or by the high temperature oxidation of nitrogen from the air used for combustion. The monoxide (NO) predominates (>90% of total NO_x) if flame temperatures are high and if quenching (rapid cooling) of the post-flame gases is avoided. This is true of most conventional combustion systems (boilers, furnaces and indirectly fired space heaters).

NO is 'insoluble' for gas sampling purposes [14], making the sample handling in these situations much simpler, provided that the small NO_2 content can be neglected, or accounted for by applying a fixed multiplier to the NO result. Inert sample lines are still required (PTFE or stainless steel at low temperature) so that NO is not lost by reaction/adsorption at the walls (particularly true of copper tubing). The NO measurement can be performed on a 'dry' basis, which is the usual legislative reference condition, thus removing the complication of calculating or measuring the water content of the sample, and correcting for any interference effects due to the presence of water vapour within the chemiluminescence analyser normally used to measure NO_x [14].

Conversely, levels of the soluble dioxide can be very high (>90%) if the cooling rate and residence time of the post-flame gases fall within certain bounds [8] or due to the presence of hydrocarbons or CO in the exhaust gas. Hydrocarbons, hydrogen and CO promote the conversion of NO to NO_2 at exhaust gas temperatures, typically less than 600°C [9]. These conditions may occur in the following systems: part load gas turbine operation [10]; co-generation systems fitted with poorly designed supplementary firing systems (in-duct burners) between the prime mover and the waste heat boiler [11]; un-flued space heaters, e.g., radiant panels [12], etc. Of course, these conditions are also produced within cooled probes extracting gas samples directly from a flame, leading to spurious results [13].

The relatively innocuous monoxide is converted to the dioxide within 15 - 30 minutes following release to the atmosphere, hence legislative limits are most often expressed as a mass based concentration of NO_2. However, this time-scale is generally longer than the time needed to effectively disperse the pollutant in the atmosphere and so the monoxide and dioxide may be treated separately when calculating the stack height required to achieve adequate dispersion [15]. A low NO_2 content could therefore be advantageous in chimney height terms but in most practical circumstances, the worst case is assumed, i.e., the emission consists entirely of NO_2, and the NO-NO_2 split is not an issue. In any case, an NO_2 content of just 3 to 9% of total NO_x is sufficient for the dioxide to dominate the stack height calculation for NO_x dispersion and, if a liquid or solid fuel is used, the resulting SO_2 emission is a more important dispersion factor [11].

However, since NO_2 is red-brown in colour, and can be seen at relatively low concentrations in large stacks, the nuisance value of brown plumes is of greater concern, particularly since emissions from combustion plant are often required to be 'colourless' [16]. An industry 'rule of thumb' states that a plume will be visible if the product of stack diameter and NO_2 emission is greater than 75 ppm.m, so, for a 3m stack, 25ppm of NO_2 is sufficient to cause visibility. This is simply a consequence of the greater optical path across the stack.

Although NO_2 is considered to be very soluble [14], there is some evidence to suggest that careful moisture removal using Peltier coolers results in very little loss of NO_2.

3.2 Sulphur based compounds

Sulphur in the fuel is oxidised mainly to the dioxide (SO_2) during combustion although a small proportion of this is subsequently oxidised further to the trioxide (SO_3). A very good estimate of the SO_x concentration can be obtained knowing the sulphur content of the fuel and the oxygen content of the stack gases, to the extent that legislation is often couched in terms of the fuel sulphur content [5]. If a direct measurement of SO_2 is required, it has a limited solubility and reasonably reliable results can be obtained after careful moisture removal [6], although heated analysers are also available [1]. Continuous analysis may be achieved by infra-red or UV absorption/fluorescence techniques.

Sulphur trioxide is highly soluble and does not exist in this free state under cool conditions (< 300°C), occurring instead as sulphuric acid vapour (H_2SO_4). The major concern within a combustion plant is to avoid the formation of the highly corrosive acid condensate produced by very low concentrations of H_2SO_4 in the vapour phase, e.g., 100ppm by weight in the vapour produces a 70% by weight H_2SO_4 condensate [7]. This is of threefold importance for gas analysis since, if the gas sample falls below the acid dew point, not only are the soluble components lost, the analyser is exposed to a corrosive agent and other insoluble sample components may react with the sulphuric acid.

4. Water Dew Point

4.1 Calculation methods

Estimation of the water dew point of combustion products is often assumed to involve a relatively complicated iterative calculation procedure. In fact, the dew point can be calculated directly knowing: the water content of the combustion products; the total sample pressure (usually atmospheric) and vapour pressure data for water.

Vapour pressure of water

For most gas sampling purposes, the saturation vapour pressure of water can be represented by the Magnus formula [17] in the temperature range 0 - 100°C:

$$\log_{10}(P_v) = \frac{Gt}{(H + t)} + I \qquad (1)$$

where
t = saturation temperature, °C
P_v = vapour pressure, mbar
G,H,I = constants (7.5, 237.3, 0.78571)

This may be extrapolated above 100°C but with increasing error; at t=151.8°C the error in P_v is less than 3% when compared with steam tables.

Since the dew point condition is met when the saturation vapour pressure equals the partial pressure of the water vapour in the sample (mole fraction * total pressure), the above formula can be re-arranged to give:

$$t_{dw} = \frac{237.3 \log_{10}(y_w P) - 186.45}{8.2857 - \log_{10}(y_w P)} \quad (2)$$

where

t_{dw} = water dew point = saturation temperature, °C
P = (known) sample pressure, mbar
y_w = mole fraction of water in combustion products

Water content of combustion products

$$y_w = \frac{(MM_{cpg}) \cdot x_w}{18} \quad (3)$$

where
x_w = mass fraction of water in combustion products
MM_{cpg} = molecular mass of combustion products ~ MM_{air} ~ 29

and

$$x_w = \frac{(WcFR + WiFR)}{(AFR + WiFR + 1)} \quad (4)$$

where
WcFR = water of combustion : fuel ratio (by mass), kg water/kg fuel
WiFR = water of injection : fuel ratio (by mass), kg water/kg fuel
AFR = air fuel ratio (by mass) =λ.AFRs
AFRs = air fuel ratio (by mass) at stoichiometric conditions (perfect combustion)
λ = air factor = excess air ratio, e.g., λ = 1.1 is equivalent to 10% excess air

The introduction of the mass, rather than the volume (molar) concentration of water actually simplifies the analysis due to mass conservation, i.e., mass of combustion products = mass of reactants (fuel + air). Stoichiometric conditions are achieved when the fuel is fully oxidised with no excess of air, e.g., UK natural gas requires nearly 10 volumes of air per volume of fuel (17 kg air/kg fuel).

By way of explanation of the terms in equation (4), the water of combustion (WcFR) is derived from the hydrogen content of the fuel and is given in Table 1 for a range of fuel types. The operating air:fuel ratio may be known directly from the measured air and fuel flows. Alternatively, the AFR can be calculated by multiplying the excess air factor, λ, by the stoichiometric AFR given in Table 1. λ is given approximately by:

$$\lambda = 21/(21 - \%O_2) \quad (5)$$

and where
$\%O_2$ = oxygen content of stack gas, % by volume, dry basis

Equation 5 holds approximately for the combustion of any fuel in air [1], certainly for the purposes of calculating dew points.

In certain circumstances, water or steam is injected into a combustion chamber in order to reduce peak temperatures and hence NO_x formation, typically in gas turbines fitted with conventional, diffusion flame burners [18]. This 'wet' low NO_x control technology, in which water:fuel injection ratios may be as high as 1:1, should be allowed for in the calculation of the dew point, hence the term WiFR in equation (4).

Example calculation

A natural gas fired boiler has a stack gas oxygen level of 3% (dry, by volume). Determine the dew point of the stack gases.

1. Calculate the air factor from equn. (5) → $\lambda \sim 1.15$, i.e., excess air of 15%
2. Calculate the mass fraction of water in the stack gases from equn. (4), where WcFR = 2.14 (Table 1), WiFR = 0 (no water injection), AFR = λ . AFRs = 1.15 * 16.6 = 19.1 (AFRs given in Table 1) →
   $x_w = 2.14/ (19.1+1.0) = 0.1065$
3. Determine the mole fraction of water in the combustion products from equn. (3) → 0.172
4. Calculate the dew point from equn. (2), knowing that the sample pressure, P, is 1013 mbar absolute, i.e., ambient pressure → dew point, $t_{dw} = 57°C$.

4.2 Variation of water dew point with fuel type and excess air level

The above equations permit the direct hand calculation of the water dew point. Figure 1 shows the variation in dew point with both fuel type and firing condition (excess air level). It can be seen that the dew point, naturally, reduces due to the dilution of excess air. For methane, the dew points falls from 60°C at stoichiometric conditions to 40°C at gas turbine exhaust conditions (15% oxygen).

The water dew point also reduces as the carbon to hydrogen ratio of the fuel increases - the lower the heating value of the fuel, the lower the hydrogen content (Table 1). The relationship for methane combustion in air represents the worst case for fossil fuel combustion in air and this can be treated as a 'universal' curve. Note, however, the higher dew points for pure hydrogen combustion and for oxy-fuel firing with methane.

To assist in the use of the of the various graphs presented here, typical flue gas oxygen contents for different combustion installations are given in Table 2, for a range of fuel types.

Because the presence of very low concentrations of sulphur trioxide causes a large elevation of the dew point (see below), the curves in Figure 1 for oil and coal combustion are largely of academic interest. The only practical application would be for fuel with a negligible sulphur content, e.g., U.K. natural gas [19]. The important point, in this case, is the reduction in the temperature requirement for the heated sample system, from, typically 180°C to 80°C. This also permits the use of a low pressure water cooled probe (temperature controlled to 80°C).

4.3 Effect of water injection

Figure 2 shows that the injection of additional water into the stoichiometric combustion products of methane - the worst case- produces a small increase in the water dew point; an injection ratio of 2:1 (water:fuel) produces a 12.5 deg.C increase in dew point.

4.4 Effect of dilution ratio

Figure 3 shows the effect of air dilution on the water dew point of fossil fuels. A dilution ratio of 30:1 is required to achieve a dew point of 0°C which would be sufficient for most sample transportation purposes. If the stack gases are already diluted due to the requirements of the process, e.g., a natural gas fired turbine with an exhaust gas oxygen content of 15% and an air factor of 3, the additional dilution required is obviously reduced, to a factor of 10 in this example.

The 30:1 dilution ratio is in line with [4] but others recommend a much higher dilution of 100:1 [1], to meet the more stringent, general, requirement of depressing the acid dew point (see below). Whilst in-situ dilution probes have the major advantage of eliminating the need for heated sample systems, the obvious disadvantages are: the vastly reduced measured concentrations, requiring ambient level analysis; the need for a separate oxygen measurement and the correction for the presence of water vapour in the sample.

4.5 Effect of pressure

The effect of pressure on dew point is shown in Figure 4. The dew point falls when the sample pressure is sub-atmospheric, typical of the majority of gas sampling systems which are operated under a weak vacuum. The high pressure data are included to indicate the importance of designing for a rapid reduction in pressure within sample probes inserted into a high pressure environment. For a cooled probe, this is also an indication of the outside skin temperature required to prevent condensation on the probe surface within the high pressure region. If water is used as the cooling medium, it must itself be pressurised to prevent internal boiling. It should be noted that, for sulphur bearing fuels, the atmospheric acid dew point is so high that it would be difficult to prevent surface condensation at high pressure.

4.6 Effect of dissolved solids

In the flue gas de-sulphurisation (FGD) systems fitted to many modern coal-fired utility boilers, the scrubbing process uses a water stream containing dissolved solids. Recent investigations [20] have shown that chloride compounds act to depress the water dew point, however, the effect is very small and can be discounted from a gas sampling viewpoint. The dew point is then simply the temperature at which the saturated gas stream leaves the scrubbing stage, say 50 to 60°C.

5. Acid Dew Point

As mentioned above, the presence of even small quantities of SO_3 (as H_2SO_4) vapour in a flue gas stream gives rise to an 'acid dew point' much higher than the equivalent water dew point. This is defined by the vapour-liquid equilibrium of the H_2SO_4/H_2O system. If an exact knowledge of the dew point is needed for process control, then this can be measured directly [21].

For gas sampling purposes, the acid dew point can be estimated as follows.

5.1 Estimation method for SO_2 concentration from fuel sulphur content

The SO_2 concentration in the flue gas stream can be calculated, from simple mass balance considerations, knowing the fuel sulphur content and the oxygen content of the stack gases. Table 3 gives the volumetric SO_2 concentration, in the wet stack gases, at stoichiometric conditions (0% oxygen) for solid, liquid and gaseous fuels. These approximations hold reasonably well across the range of liquid fuel and coal types (+/-10%). The concentration can then be adjusted to the actual

combustion conditions by dividing by the air factor, λ, to account for the dilution due to excess air, remembering that λ can be derived from the stack gas oxygen content (Equation 5).

5.2 Estimation method for SO_2 conversion to SO_3

The chemistry of SO_2 oxidation is discussed by Williams [22] who recommends an equilibrium constant for the reaction $SO_2 + 0.5\ O_2 = SO_3$ which dominates at high temperatures. Unsurprisingly, the concentration of SO_3 increases with increasing excess air (proportional to $[O_2]^{0.5}$). Depending on the process conditions, it is not always obvious how to determine the most appropriate temperature and oxygen content for these calculations. The situation is further complicated by the increased conversion due to catalysis, promoted by the heavy metal content of some fuel oils and petroleum coke, particularly the vanadium content [23, 24].

Oil firing therefore generally produces a greater proportion of SO_3 than coal firing. For oil combustion, the maximum conversion rate quoted in the literature varies considerably: 3% [22]; 5% [23] and 8% in diesel engine exhausts [24]. A figure of 10% is therefore recommended for scoping calculations but it must be recognised that this is pessimistic assumption.

Coal firing produces SO_3 conversion rates of the order of 0.5% [27] ; a figure of 1% is therefore recommended for scoping calculations. In the absence of specific data for gaseous fuels, a figure of 1% is suggested, since catalytic components are not present in the fuel.

The fraction of SO_2 converted to SO_3 is denoted by F_{SO3} and this is equal to 0.01 for coal / gaseous fuels and 0.10 for oil firing.

5.3 Calculation method for the acid dew point from SO_3 concentration

A semi-empirical correlation, for calculating the acid dew point from the concentrations of SO_3 and water in the gas stream, was developed by Banchero and Verhoff [28] who concluded, in 1975, that the thermodynamic phase equilibrium data of the time were not sufficiently accurate to enable an entirely theoretical approach to be used. They developed a correlation of the form:

$$1000/t_{da} = A + B.\ln(p_{acid}) + C.\ln(p_w) + D.\ln(p_w).\ln(p_{acid}) \qquad (6)$$

where

t_{da} = acid dew point, **K**
p_{acid} = partial pressure of the acid component in the gas stream, mm Hg
p_w = partial pressure of the water in the gas stream, mm Hg

and A, B, C & D are constants given in Table 4. The partial pressure of water is determined knowing the mole fraction of water and the total pressure, as described above. Similarly for the acid component; the mole fraction of H_2SO_4 is equivalent to the volume concentration of SO_3. Equation (6) is valid for a dew point range of 100 - 230°C at a stated accuracy of +/- 8 deg.C. The same form of equation has been used to correlate dew point data for a number of other acid components, as defined in Table 4, to a claimed accuracy of +/- 6 deg.C [29].

Figure 5 shows the acid dew point as a function of SO_3 (H_2SO_4) concentration for a range of water contents. There are a number of important points to note. Firstly, for a given SO_3 concentration, the acid dew point is relatively insensitive to water content in the range describing most combustion processes and fuel types (5 - 20% water content), the variation being about 10 deg.C. This suggests the use of a single, 'worst case' curve, at 20% water content, giving:

$$t_{da} = 9.4352.\ln([SO_3]) + 125.19 \qquad (7)$$

where

t_{da} = acid dew point, **°C**
$[SO_3]$ = SO_3/H_2SO_4 concentration in ppm by volume, wet basis

Secondly, the acid dew point is significantly higher than the water dew point at very low concentrations of SO_3, 0.1ppm giving 100°C, compared with about 60°C for the water dew point. Significant dew point elevation can therefore result from very modest amounts of sulphur in the fuel. Very high dilution levels are required to reduce the SO_3 concentration to suitably low levels.

Thirdly, it should be noted that the Banchero-Verhoff correlation cannot be extrapolated safely beyond its stated range of application. At SO_3 contents below 0.1ppm (acid dew point<100°C), the value of t_{da} does not approach the water dew point. Okkes [30] suggested an alternative form of relationship for enhanced accuracy at low dew point temperatures, however, this does not give sensible results at very low SO_3 concentrations.

A more practical approach would be to assume a conservative acid dew point of 100°C for $[SO_3]$ < 0.1ppm. Alternatively, the combination of improved thermodynamic data and computing power has enabled the direct calculation of t_{da} across the full range of conditions [20, 26].

5.4 A simple expression for acid dew point

Combining the above equations, to obtain a simple expression for the acid dew point, we obtain:

$$t_{da} = 9.4352 \ln\{\%S.(F_{SO2}/\lambda).F_{SO3}\} + 125.19 \quad (8)$$

Defining all of the terms again:

%S = sulphur content of the fuel, % by mass
F_{SO2} = concentration of SO_2 in the wet stack gases at stoichiometric conditions
= (ppm by volume, wet basis)/(%S in fuel)
= 920, 600, 475 for coal, oil and natural gas respectively
λ = air factor ~ $21/(21-\%O_2)$
$\%O_2$ = oxygen concentration
F_{SO3} = fraction of SO_2 converted to SO_3
= 0.01, 0.10, 0.01 for coal, oil and natural gas respectively

So, a conservative estimate of the acid dew point can be determined knowing only the fuel type, the fuel sulphur content and the oxygen content of the stack gases. This equation applies at atmospheric pressure.

Figure 6 illustrates the application of Equation 8 to utility boiler firing in which the dew point is given as a function of fuel sulphur content. Coal and gas produce similar results but it must be remembered that the sulphur content of natural gas is usually negligible and it is more appropriate to use the water dew point. The dew point for coal firing lies in the range 140 to 160°C for realistic fuel sulphur contents. As expected, oil firing gives the highest dew point - up to 180°C. As might be expected, these are within the limits of PTFE heated systems (~200°C).

5.5 Other acid components

A dew point correlation can be developed for any other soluble 'acid' component, as described above, with reference to Table 4. Other components, such as NO_2 and halides, do not significantly raise the 'worst case' water dew point of 60°C at the concentration levels normally found in stack gases. In complex mixtures, the effect of components other than sulphuric acid will tend to reduce the mixture dew point, resulting in a greater margin on the acid dew point as calculated above.

6. Partition between NO and NO_2

Chemiluminescence analysers measure the total NO_x and, optionally, the NO content, enabling the NO_2 to be determined by difference. When the NO_x is measured, the sample is passed through a heated reaction chamber, the 'converter', in order to reduce any NO_2 present to NO.

Usually, the total NO_x is measured and reported, unless there are particular reasons for determining the NO/NO_2 split. In some combustion systems, the split can provide useful information about the process, particularly the ingress of unwanted air into the main combustion zone. More commonly, it is needed for proving trials in which it can be demonstrated that the NO_2 content can be neglected, making the gas sampling and analysis task much easier. Once demonstrated, the emphasis must then be placed on preventing any change to the split between NO and NO_2 within the sample train. Finally, the NO/NO_2 partition may be important for plume dispersion calculations.

The importance of selecting inert material for transfer lines has already been emphasised. Not doing so can result in the loss of NO_x (by reaction/adsorption at the wall) and/or the conversion of NO_2 to NO (catalytic reduction at the wall). Where possible, PTFE components are used, however, it is also common practice to use stainless steel tubing at 'low' temperatures (<200°C) and as an un-cooled stack sampling probe material for temperatures up to ~600°C. Stainless steel is used for the construction of converters in some chemiluminescence analysers, demonstrating its activity as a reducing catalyst.

Un-cooled steel sample probes promote almost total conversion of NO_2 to NO at temperatures above about 300°C [31]. This is acceptable, provided that the NO/NO_2 split is unimportant. Otherwise, an inert probe material, such as quartz, must be specified [32] or a cooled steel probe, provided that the internal surface temperatures are carefully controlled. In the case of the cooled probe, the temperature must not be allowed to drop below the dew point.

Below 300°C, the surface activity of steel falls off rapidly. Below 100°C, the conversion is negligibly small [31]. In the region 100 - 200°C (required for sulphur containing fuels) conversion rates are low but, given the potential sensitivity to ageing and surface finish effects, reported in the literature, it is good practice to minimise the wall temperature. This conflicts with the general practice of maintaining the highest temperature available (200°C) but, practically, there is little that can be done apart from minimising surface contact area and, where the dew point allows, reducing wall temperatures.

7. In-flame sampling

The extraction of in-flame gases is much more demanding than stack gas sampling and cannot be treated fully here. However, there are a few points worth noting. The main requirement is to quench the combustion reactions so rapidly that the sampled composition is the same as that at the measurement point. Schoenung & Hanson [33], amongst others, showed that wall cooling generally provides an insufficient quench for accurate CO measurement. A pressure quench is much more effective, i.e., the rapid reduction in pressure to a very low absolute level within the probe. In their study, the measured CO approached the true value at pressures < 100mbar absolute.

As mentioned earlier, parallel studies have shown that NO can be converted to NO_2 within the sample probe [34] due to the rapid thermal quench. Again, this false NO_2 split can be avoided by using a pressure quench but it must be recognised that this places much greater demands on the design of both the probe and the sampling system [35].

8. Concluding remarks

Simple equations for the direct calculation of the water and acid dew points of stack gas samples are presented. These are suitable for the scoping calculations required for gas sample handling design. Specimen calculations explore the sensitivity of dew point to fuel type, operating conditions and acid components.

Fossil fuels with a negligible sulphur content produce stack gases with a worst case water dew point of 60°C, assuming that additional water is not injected into the combustion chamber. This enables the use of low pressure water as a sample probe coolant and avoids the distortion of the NO/NO_2 split which is important when considering a) the combustion process, b) exhaust plume dispersion and c) the complexity of the sample handling (when the soluble NO_2 component is small, the transfer lines can be unheated).

Sulphur bearing fuels produce atmospheric dew points in the range 130 to 180°C in most practical situations. When sampling from a high pressure environment, care should be taken to ensure that the pressure is reduced on entry into the sample probe.

Sample line and probe temperatures should be minimised in order to minimise the conversion of NO_2 to NO in the sample train.

Conventional probe cooling is insufficient to obtain reliable results when sampling from within flames. Rapid pressure reduction, to a low absolute pressure level, is required to ensure that CO measurements are representative and that the true NO/ NO_2 split is preserved.

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Table 1 Combustion properties for a range of fuel types

Fuel	C:H ratio	WcFR (kg / kg fuel)	AFRs	
Hydrogen	0.0	9.00	14.50	
Methane		3.0	2.25	17.30
UK natural gas	3.1	2.14	16.61	
Light distillate	5.3	1.41	15.09	
Gas Oil	6.5	1.18	14.44	
Heavy fuel oil	7.5	1.02	13.84	
High volatile coal		16.5	0.46	9.74
Anthracite	32.5	0.28	9.84	

C:H ratio = carbon:hydrogen atomic mass ratio ratio
WcFR = water of combustion:fuel mass ratio
AFRs = air:fuel ratio at stoichiometric conditions

Table 2 Stack gas reference oxygen content

Process	Fuel type	Oxygen content (% by vol. dry basis)
Utility boilers & Furnaces	Nat. Gas	3
	Oil	3
	Coal	6
Gas turbines	Nat. Gas	15
	Gas oil	15
Compression Ignition Engines	Nat. Gas	15
	Oil	15
Incineration	Various	11

Table 3 SO_2 emissions at stoichiometric conditions as a function of fuel type

	F_{SO2} (ppm SO_2 wet) / (% S by mass in fuel)
Coal:	920
Oil:	600
Natural gas:	475

Table 4 Acid dew point - constants for use in Equation 6

Acid	A	B	C	D
Sulphuric	2.2760	-0.0294	-0.085800	0.006200
Sulphurous	3.9526	-0.1863	0.000867	-0.000913
Nitric	3.6614	-0.1446	-0.082700	0.007560
Hydrochloric	3.7368	-0.1591	-0.032600	0.002690
Hydrobromic	3.5639	-0.1350	-0.039800	0.002350

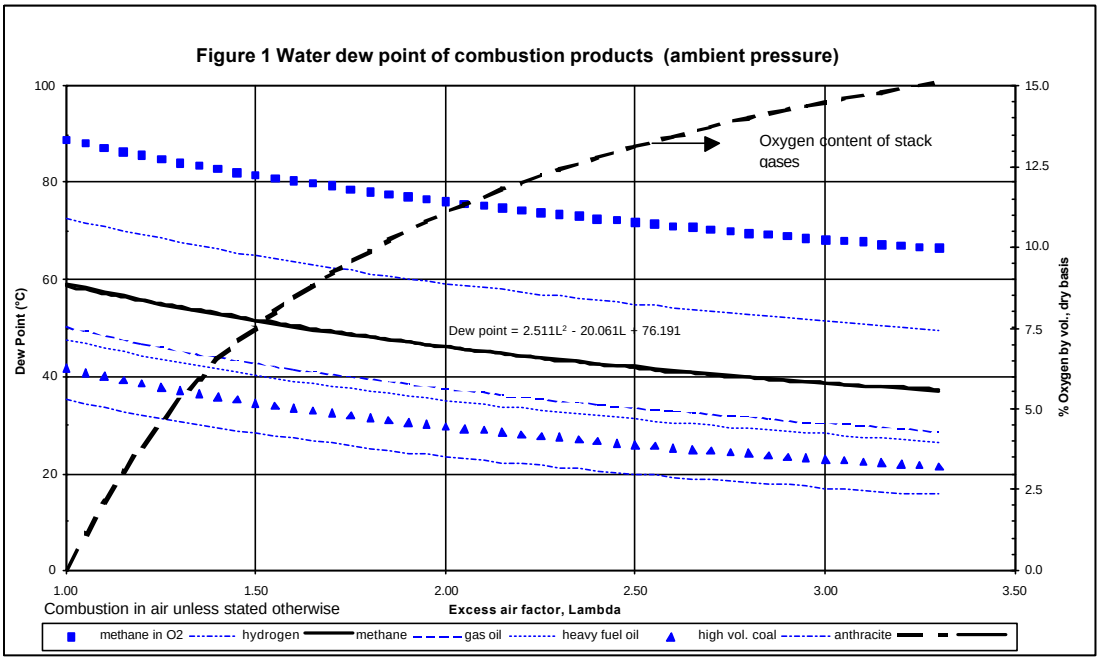
Figure 1 Water dew point of combustion products (ambient pressure)
Oxygen content of stack gases
Dew point = 2.511L² - 20.061L + 76.191
Dew Point (°C)
% Oxygen by vol., dry basis
Combustion in air unless stated otherwise
Excess air factor, Lambda
methane in O2
hydrogen
methane
gas oil
heavy fuel oil
high vol. coal
anthracite

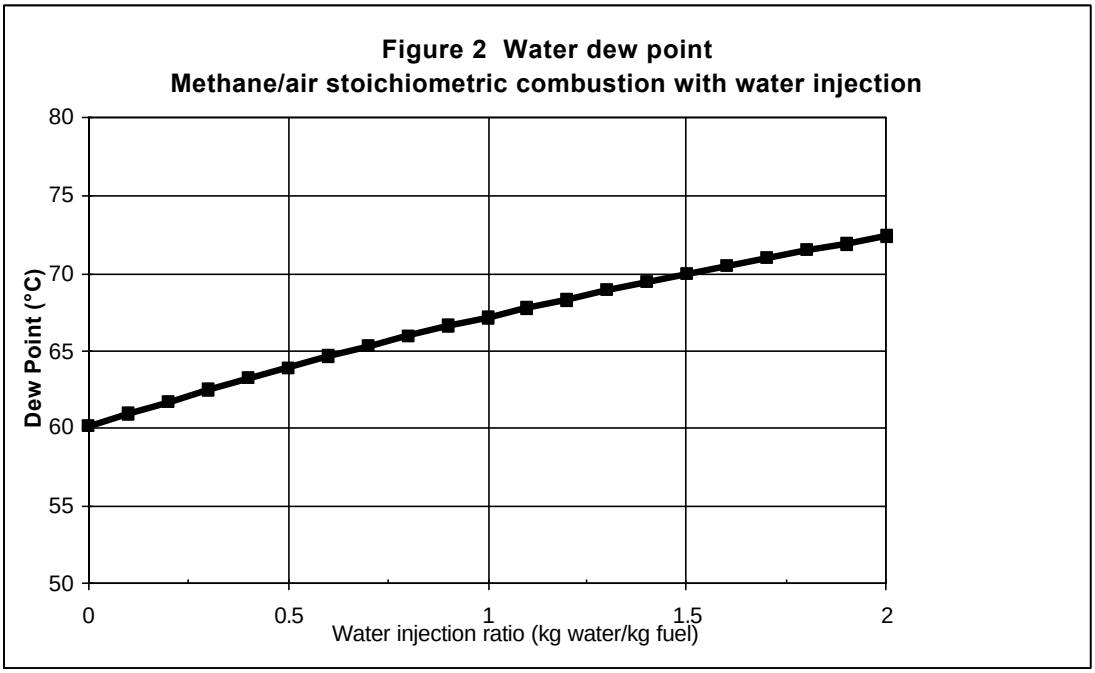
Figure 2 Water dew point
Methane/air stoichiometric combustion with water injection
Dew Point (°C)
Water injection ratio (kg water/kg fuel)

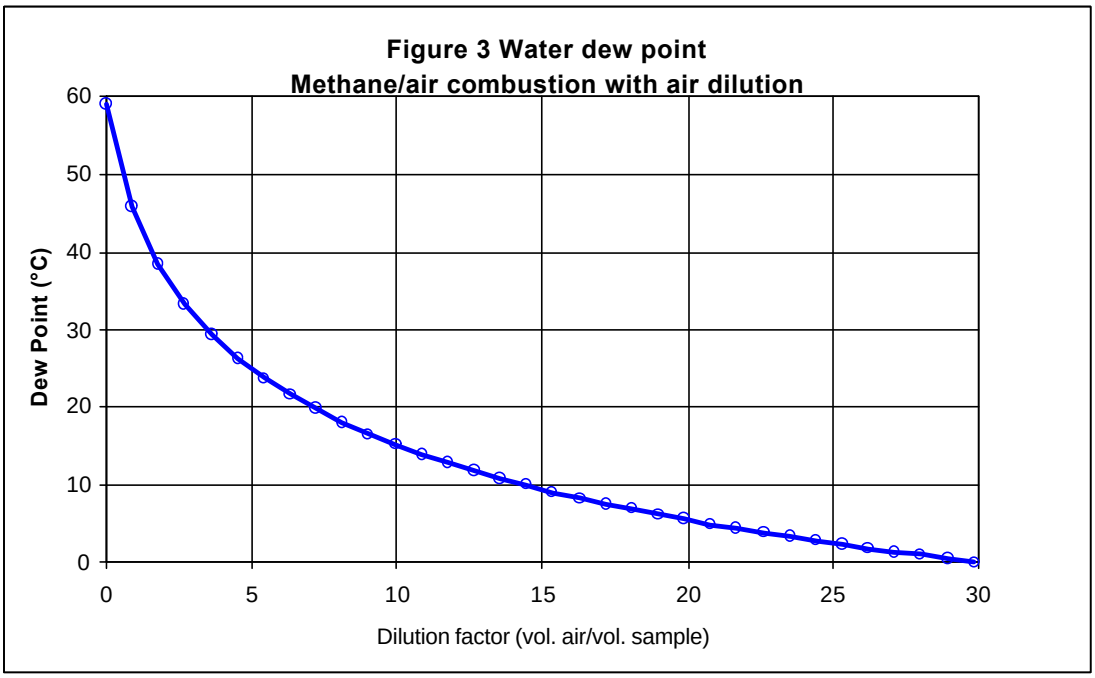
Figure 3 Water dew point
Methane/air combustion with air dilution
Dew Point (°C)
60
50
40
30
20
10
0
0
5
10
15
20
25
30
Dilution factor (vol. air/vol. sample)

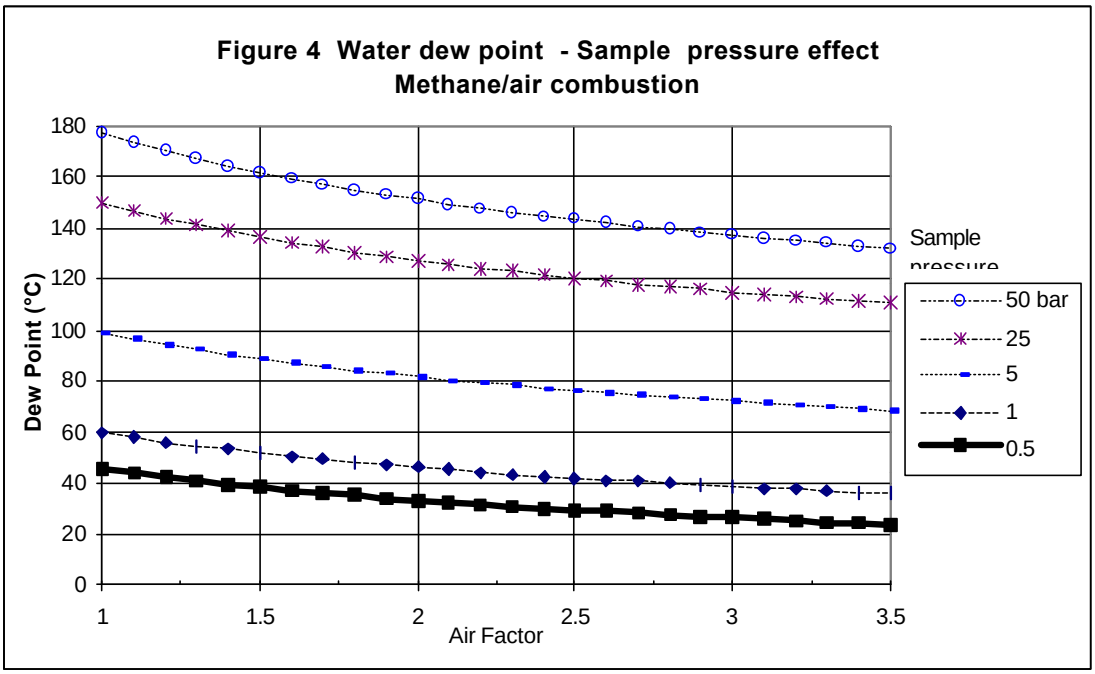
Figure 4 Water dew point - Sample pressure effect
Methane/air combustion
Dew Point (°C)
180
160
140
120
100
80
60
40
20
0
1
1.5
2
2.5
3
3.5
Air Factor
Sample
50 bar
25
5
1
0.5

Figure 5 Sulphuric acid dew point (Banchero & Verhoff)

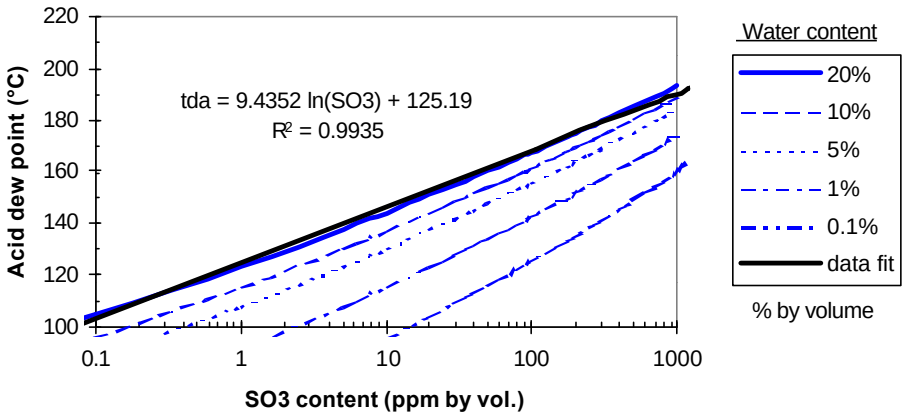
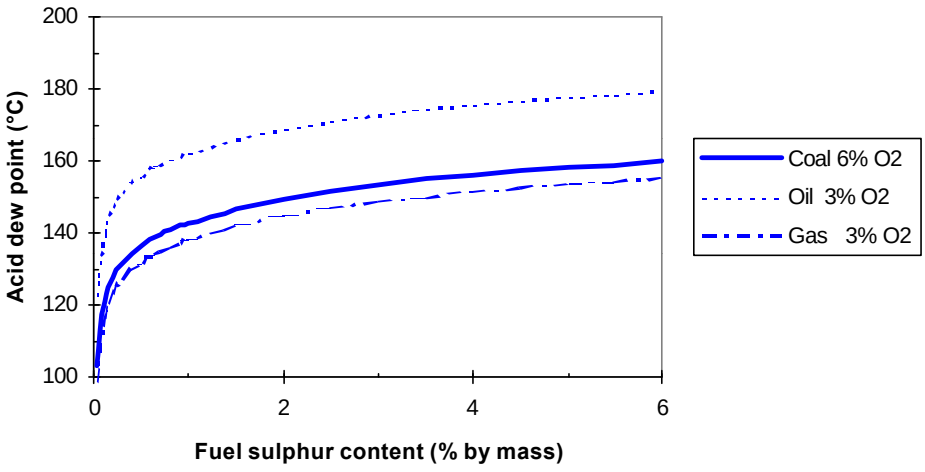
Figure 6 Acid dew point for utility boilers