

## **IMPLEMENTATION OF GAS CONCENTRATION MEASUREMENT SYSTEMS USING MASS SPECTROMETRY IN CONTAINMENT THERMAL- HYDRAULICS TEST FACILITIES: DIFFERENT APPROACHES FOR CALIBRATION AND MEASUREMENT WITH STEAM/AIR/HELIUM MIXTURES**

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### **KEY WORDS**

thermal-hydraulics, containment, test facility, gas concentration, mass spectrometry, calibration, water vapor.

### **ABSTRACT**

Thermal-hydraulic test facilities are used to investigate various containment phenomena such as, for example, mixing and stratification of gases or steam condensation in the presence of noncondensibles. Experiments are also required for validation of codes possessing capabilities for modelling such three-dimensional effects. The need for advanced instrumentation allowing to measure gas concentration in such conditions (typically: 100-180°C; 1-10 bar) and to get sufficiently refined information about spatial distribution of the different gas species has become apparent. This paper deals with the implementation of gas analysis systems using some commercial Quadrupole Mass Spectrometers (QMS) that have been recently added to the basic instrumentation in three thermal-hydraulics test facilities namely MISTRA (CEA, France), TOSQAN (IRSN, France) and PANDA (PSI, Switzerland). In recent years, QMS have increasingly been selected for various applications because of attractive metrological characteristics (sensitivity, span of concentration range, response time, stability, etc.), relatively compact size and low

cost. Although commercial QMS are sold as “turnkey” systems, these instruments are delicate to bring into operation. As QMS are not absolute instruments, reliable calibration procedures are required for quantitative measurements. A mass spectrometer can be regarded as an ionisation gauge with subsequent separation system for the different ion species. The calculation of gas concentrations considers the partial pressure of a particular gas species to be proportional to the ion current it generates. Anyway, one must know the QMS sensitivity to the gases of interest and the only practical method is to use calibration gases. Calibration must be carried out using mixtures whose compositions are close to any possible sample compositions and the procedure selected should duplicate as closely as possible the measurement conditions established during the real experiment. This work concerns measurement of steam-air-helium mixtures of any composition distributed in pressurized vessels. The developed systems provide concentration point measurements at typically a few tens of different locations in the facility vessels. This paper will give an overview of the three different measurement systems and will address the main difficulties encountered to develop these systems such as those related to the sample pressure reduction or to the presence of water vapor. The paper focuses on different attempts and approaches to generate the calibration gas mixtures containing water vapor and calibrate the QMS. Even if the calibration procedures still have to be improved, some recently acquired data are here to prove the promising achievements of the technique.

## **1. INTRODUCTION**

### **1.1 Background**

In the area of containment thermal-hydraulics, development of codes possessing 3D capabilities is needed to address safety issues of current or future reactor types. These codes have to be validated with respect to identified phenomena important for simulation of containment thermal-hydraulics such as wall condensation, gas stratification, natural circulation, turbulent diffusion, and interaction between these phenomena. However, an adequate experimental database is required in order to validate the new capabilities. The MISTRA, TOSQAN and PANDA facilities are currently participating in a number of national and international projects carried out with the goal to offer an enhanced database for the validation of advanced codes (Yadigaroglu, 1998, Studer, 2003, Vendel, 2003). With respect to these objectives, the need for more refined information about gas distribution in the facilities has become apparent. The idea of using Mass Spectrometry to retrieve gas concentration was thus considered and adopted in the three facilities.

Mass Spectrometry is a well-proven analytical technique used in vacuum research applications for a few decades. In recent years, the QMS has increasingly been used in new applications away from vacuum technology, often with the demand for quantitative results. The main difficulties related to this special application of mass spectrometry will be outlined in this paper.

### **1.2 Presentation of the three facilities**

PANDA is a large-scale thermal hydraulic test facility designed and used for investigating containment system behavior and phenomena for different Advanced Light Water Reactors designs and performing large-scale separate-effect tests (Yadigaroglu, 1998). When, for example, the containment of a European Simplified Boiling Water Reactor (ESBWR) is considered, PANDA scales heights approximately 1:1 and decay power and volumes 1:40 with respect to the reactor. The facility consists of large interconnected vessels and open water pools (figure 1). The total volume of the gas spaces of interest (where gas concentrations have to be measured) is about 320m<sup>3</sup>. PANDA instrumentation consists of numerous sensors for the measurements of fluid and wall temperatures, total and air partial pressures, flowrates, phase indications, valve states and heater power (Huggenberger, 1996). As an example, a test series has recently been performed in the PANDA facility in the frame of the 5th European framework

program project ‘TEMPEST’ (Auban, 2003). The objective of these tests was firstly to assess the influence of light gases on Passive Containment Cooling Systems designed for the ESBWR. The release of a large amount of hydrogen in the course of the transient was considered and simulated by an helium injection in the PANDA facility. Another important objective of this kind of test was to provide relevant data about gas mixing and stratification in large volumes for testing capabilities of modern —mainly Computational Fluid Dynamic (CFD)— codes. Some gas concentration measurements acquired during this test series will be presented in this paper.

The MISTRA facility is devoted to containment thermal-hydraulics flows involving natural or mixed convection. The vessel is a cylinder of 4.25 meters in diameter, 7.3 meters in height and a volume of about 100 cubic meters. The steam and non-condensable gases are introduced through a nozzle located at the bottom of the containment (previously located at the centre, and now on a moving rail for off-centred injections). Three thermally-regulated condensers control the steam condensation. The measurements mainly consist in establishing velocity (LDV), temperature and concentration spatial mappings suitable for CFD code validation. The MISTRA facility became fully functional in 2001, and a series of tests was performed over the period 2001 to 2003, including air/steam and air/steam/helium tests (such as ISP-47) for the validation of the TONUS code (Studer, 2003 and Beccantini, 2003), and air/steam/helium/nitrogen tests for the validation of the NAUTILUS code (Magnaud, 2003). A detailed description of MISTRA facility and instrumentation is given in a companion paper (Studer, 2003).

The main purpose of the TOSQAN experiment is to validate the condensation and flow models incorporated in multi-dimensional Computational Fluid Dynamics (CFD) softwares such as the TONUS code (see Cornet 2002, Malet, 2001). This validation is performed for various thermal-hydraulic conditions representative of severe accidents of a Pressurized Water Reactor (PWR), i.e. for turbulent flows in natural, mixed and forced convection regimes and in the presence of non-condensable gases. Special attention has been paid to local measurements, which will allow the principal variables under study (temperature, concentration and velocity) to be correctly mapped. The TOSQAN enclosure is a cylindrical chamber of stainless steel size (1.5m i. d., and 4.8m height) and includes a sump (figure 13). Its walls are thermostatically controlled so that condensing and non-condensing surfaces can be obtained. The relatively small volume (7m<sup>3</sup>) of the facility, its rather simple geometry and the possibility to achieve well-defined boundary conditions make the use of the TOSQAN data for CFD validation purpose realistic.

## **2. PRESENTATION OF THE TECHNIQUE**

### **2.1 Basics**

It is essential to have a clear idea of how the QMS is measuring gas concentrations (mole fraction in the gas sample) and to be aware of some of the system limitations. The principle of the technique is outlined in this section. This kind of analyzer consists in an inlet system, an ion source, an analyzer and a detector (Lafferty, 1998; Hoffman, 1998). The inlet system converts the sample pressure to a vacuum level acceptable for ionization and directs the sample towards the ion source. Electron impact is the most widely used method for ion generation: in this source, a filament is heated to a temperature high enough for thermo-ionic emission. The emitted electrons, after acceleration, are able to form ions from neutral species present so that they can be separated by electric or magnetic fields. The analyzer, which is a quadrupole mass filter separates the ions according to their mass-to-charge ratio. A spatial separation occurs, ions created at the same time being made to travel on various trajectories according to mass-to-charge ratio. Ions with trajectories leading to the detector provide an ion signal, others are lost. After electrical amplification, the measurement signal appears as a current  $I$ . So, the first point to make is that the QMS calculates gas concentrations from these measured ion currents.

Using the relation characterizing the ionization process and the equation of state, the following basic

relation can be derived to express the ion current as a function of pressure  $p$  (Grosse Bley, 1998):

$$I = \bar{S}p \quad (1)$$

where  $\bar{S}$  is the effective sensitivity of the system with the dimension  $\text{Amp.mbar}^{-1}$ . The sensitivity will mainly depend upon the different gas species, geometry and emission current of the respective system.

From relation (1), the relation between the ion current (the peak height) at mass number  $M$  (more exactly, mass-to-charge ratio) produced by gas  $G$ ,  $I(G,M)$ , and the partial pressure  $p(G)$  can be written as follows:

$$p(G) = \frac{I(G,M)}{S(G,M)} \quad (2)$$

This is the basic equation for evaluation of partial pressures of a gas  $G$  out of measured ion currents at mass numbers  $M$ . The following relation shows the dependencies of the sensitivity  $S(G,M)$ , on the different processes happening in the ion source and the quadrupole mass filter:

$$S(G,M) = S_0 \cdot IP(G) \cdot FF(G,M) \cdot T(M) \quad (3)$$

The ion source together with the collector, determines the basic sensitivity,  $S_0$ , which is normally stated for an inert gas such as nitrogen. The three other quantities are:

$IP(G)$ , ionization probability for gas  $G$  ('How easy is it to make an ion?');

$FF(G,M)$ , fragmentation factor of gas  $G$  at mass number  $M$  ('How many fragments are produced and what is the amplitude of each?');

$T(M)$ , relative transmission at mass number  $M$  ('How many ions actually reach the detector?').

The complete formula expressing the partial pressure out of an ion current reading at mass number  $M$  of a QMS has to be written as:

$$p(G) = \frac{I(G,M) - I_0(M)}{S(G,M)} = \frac{I(G,M) - I_0(M)}{S_0 \cdot IP(G) \cdot FF(G,M) \cdot T(M)} \quad (4)$$

with  $I_0(M)$  being the offset current at mass number  $M$  not resulting from the observed mass peak.

As the underlying assumption in deriving the concentration is that there is a linear relation between the partial pressure and the corresponding signal (ion current), the linearity of the QMS should be tested to establish the pressure range in which such a linear relationship holds. For reliable quantitative measurements, for each gas, the range of pressure in which no deviations from linearity occurs has to be found out by some preliminary testing. One can test different pure gases by measuring the ion current over a range of pressure within the QMS. Thus, some QMS settings can be tuned to get a better linearity. As an example, the electron emission current characterizing the source operation (ionization) can be lowered. Typically, this linearity is valid over two decades of pressure for an appropriate pure gas (Ellefson, 1987).

The calculation of gas concentrations considers the partial pressure of a particular gas species to be proportional to the ion current it generates. Thus the concentrations in a mixture of gases are found by comparing the relative strengths of the ion currents. But for this, one must know the QMS sensitivity to the gases of interest. It must be explained why the only practical method for this is to use a calibration gas. The ion currents measured during a special calibration routine combined with the fact that the composition of the mixture is known, provide calibration coefficients (that are essentially relative sensitivities, see below). This procedure allows one to measure gas concentrations without knowing the total pressure or any partial pressures within the QMS itself.

At high sample pressure (compared to usual vacuum applications, i.e.  $>10^3$  Pa), the application of a fixed orifice has to be used to reduce the sample pressure. In this case, the flow in the orifice will certainly be in the viscous range whereas the flow out of the ionizer should be in the molecular range. Since the viscous flow will carry each component uniformly without altering the gas composition, while the molecular flow will preferentially carry out the lighter components, fractionation will occur. That is, the partial pressure composition in the QMS differs from that at the sampling location by factors related to the molecular weights of the different components. Fractionation must be accounted for in calculating

the gas composition (see equation (4)), or calibration must be performed with a mixture whose composition is close to the sample composition, at similar sample and analyzer pressures. In that case the effect of fractionation will be “buried” in the calibration factor together with the various ionization and detection probabilities of the different species. Another problem is that the presence of one gas can influence the sensitivity to another. To summarize, it is required to use a set of calibration gases. Each calibration gas should allow to measure the resultant QMS ion currents for a known composition at the sample inlet. The calibration procedure should duplicate the measurement procedure (pressure, temperature, configuration of inlet and vacuum systems, QMS settings...) as closely as possible, using predefined mixtures.

Calibration method for concentration measurements (without peak superposition):

The following relations depict the simple case for which each component is represented by an ion current from a single mass-to-charge ratio. No overlapping of peaks in the mass spectrum has to be considered. In principle, the concentration (volume or molar fraction)  $x(G)$  is given by:

$$x(G) = \frac{p(G)}{P_{\text{total}}} = \frac{p(G)}{\sum_g p(G)} \quad (5)$$

Using the basic relation (2) between partial pressures and measured ion currents, one can simply write the following ratios, written in the case where three components (for which 1, 2 and 3 subscript numbers are used) are involved:

$$\frac{P_2}{P_1} = \frac{S_1 I_2}{S_2 I_1} ; \frac{P_3}{P_1} = \frac{S_1 I_3}{S_3 I_1} \quad (6)$$

These ratios can be written using relative sensitivities  $S'_2$  and  $S'_3$  :

$$\frac{P_2}{P_1} = \frac{1}{S'_2} \frac{I_2}{I_1} ; \frac{P_3}{P_1} = \frac{1}{S'_3} \frac{I_3}{I_1} \quad (7)$$

with  $S'_2 = \frac{S_2}{S_1}$  and  $S'_3 = \frac{S_3}{S_1}$

The calibration process will consist in calculating these calibration coefficients  $S'_2$  and  $S'_3$  from measured ion currents and knowing the composition of the calibration gas but not the partial pressure. This calibration method is based on the omnipresence of one gas (in PANDA, nitrogen was used). All ion currents are compared to the current from the standard gas (here, it is nitrogen), without which you would not be able to make the concentration measurement.

The question ‘How often do I have to calibrate?’ may be asked. The answer is related to stability, which refers to the constancy of sensitivity over a period of time. Gas mixtures with major components (>10mol%) should be regularly analyzed to monitor the validity of the set of sensitivities (Ellefson, 1987). Contamination in the source or the analyzer, or shifts in electric supply voltages are the major causes of its degradation with time and use. However, the calibration procedures that are used profit from the fact that the ratios of sensitivities can be at least one order of magnitude more stable than the sensitivities themselves as the consequences of all possible drifting effects are minimized.

A point to keep in mind is that calibration with a gas mixture provides relative sensitivities to the test gases for one specific gas composition and pressure within the QMS. But when measuring an unknown gas, the composition is (naturally) not the same as the calibration gas and so the effective sensitivity is somewhat different, leading to measurement error. Also, if the pressure within the QMS is allowed to vary, the measurement accuracy will be affected. The accuracy can be tested by calibrating with a particular gas mixture and then measuring others mixtures and noting the resultant errors. Due to the large range of possible concentrations that must be measured, e.g. 0-100% for each gas species, it is realized that high absolute accuracy is not possible. But measurement accuracy within a few percent of the measured value is expected.

A lot of recommendations can be given to calibrate a QMS (Basford, 1993), and notably concerning precautions to observe before calibration. Of course, the vacuum pumps, heating systems should be started a long time (days) before starting any measurement. The instrument itself should be warmed-up (filament and electronics) to a stable operation condition. Tuning the QMS mass scale (in the adequate range) is also a necessary fast operation to be repeated regularly.

## **2.2 Some difficulties to implement a QMS in a thermal-hydraulics test facility**

### **2.2.1 Design of the inlet system**

One first difficulty is that these systems should be able to bring the sample from a pressurized vessel up to the analyzer chamber where low vacuum conditions are established. The QMS is intrinsically a vacuum instrument that operates at best near  $10^{-6}$  mbar. Above  $10^{-5}$  mbar the response becomes non-linear and above  $10^{-4}$  mbar the filament will be shut off by the control electronics. To sample gases at higher pressures, the design of an adequate pressure reduction system is required. These systems basically use restrictions (capillaries, pinholes...) and vacuum pumps. At pressures corresponding to our applications, a two stage reduction based on a capillary and aperture is used. The design of the inlet system is important, notably to minimize response times. Any dead volume on the high-pressure side of the aperture causes a larger response time. To achieve a fast response time and minimize fractionation, a capillary inlet is used with by-pass pumping as shown in figure 2. The sampled gas is drawn through the capillary most of it is bypassing the analyser to be exhausted by the vacuum pump. Only a small amount of the flow is diverted to the QMS through an aperture. This continuous renewal of the gas sample along with the orifice operating in the molecular flow range makes this method attractive, since through this arrangement much higher sample flow can be attained than if the capillary would lead directly into the ionizer. Response times are in the order of seconds or less (Hoffman, 1998). The second method to decrease the response time is to ensure that the gas is travelling at significant velocity so that proper lay-down of the inlet tubing will use the kinetic energy of the sampled gas to mix the dead volume. Some information about the sampling and inlet systems used in the three test facilities will be given in later sections (2.2.3 and 4.1).

### **2.2.2 Presence of water vapor**

The designed gas concentration systems should be able to function with any fraction of vapor in the analyzed gas mixture (0-100% vol.). It was often emphasized that analysis of water in vacuum systems presents large difficulties (Primiano, 1984; Berman, 1996) and literature about quantitative measurements in presence of water vapor is relatively scarce. First, very slow rates of removal by the vacuum pumps have to be expected because of the ability of water to adsorb tightly to almost every surface it impacts. One consequence of the peculiar properties of water concerns the response time of the measurement system. It was always found that the step-response for water vapor could be on the order of seconds for this kind of commercial QMS.

Moreover, exposure of QMS to water can cause instabilities to their sensitivities to all gases. Some effects of high water partial pressure have already been observed (Basford, 1994). Some reaction with the metals of the hot filaments in the source can affect the ionization efficiency, decreasing the emission current and thus the QMS sensitivity.

Finally, the technical difficulty to generate different gas mixtures (of known composition) containing water vapour for the calibration of the instrument has to be pointed out and will be outlined in this paper. This, in a large extent, explains difficulties in calibrating and assessing the measurement accuracy of the technique.

Of course, the presence of steam makes also the design of the whole sampling and measurement system a little more delicate as any problems due to steam condensation must be avoided.

## 2.3 Different purchased QMS

In PANDA, a QMS HAL 201-RC was purchased from Hiden Analytical Limited (England). Signals are acquired on a PC, using the software from Hiden. The concentrations are processed (with Matlab) from the ion currents data after a test using adequate coefficients derived from pre-test calibrations. Concerning the inlet system, this QMS is equipped with a Quartz inert capillary (2m, heated at 150°C) with platinum orifice molecular leak and a by pass pumping line (rotary pump) equipped with a precision sample by-pass control valve. A suitable pressure should be kept at the inlet of the capillary (in the 100-200 mbar range). In the source, a twin filament made of oxide-coated iridium is used. The pressure within the QMS is measured with a Compact Cold Cathode Gauge (IKR261 from Pfeiffer Vacuum). This kind of ionization gauge is highly gas dependant. According to Pfeiffer, for pure gases below  $10^{-5}$  mbar, the actual pressure can be determined by using a multiplicative correction factor (different for each species). Anyway, this gauge is not very accurate (+/-30%) and this measurement in case of gas mixtures can only be considered as a rough estimation of the pressure within the QMS. Penning Gauge and interlocks are only used to provide protection for the mass spectrometer in the case of over pressure. In other words, a partial pressure analysis can't be based on this measurement. As a detector, a faraday cup is used principally because a SEM detector cannot withstand a pressure range as wide as a faraday cup. Moreover, there is no absolute need for our application to get a much better sensitivity using a SEM detector.

In MISTRA, a QMS 'transpector2' from Inficon is used. The instrument is controlled by a PC, using RS232 connection (or RS485 connection in case of multi-sensor use), and is operated by the software from the same company ('TranspectorWare'). Gas introduction into the sensor is specially designed to avoid segregation effects, and the sensitivities for the gases of interest can be checked during the tests in order to determine if a new calibration procedure is necessary (Brinster, 2002). The concentrations are processed from the ion currents data after a test using Matlab.

In the TOSQAN facility, a FABSTAR QMS was purchased from Inficon (figure 13). It consists of a complete sampling system composed of an introduction capillary of 0.15mm i.d. thermo-regulated at 200°C, a 15µm i.d. diaphragm, a differential pumping system heated up to 200°C, a measurement chamber and the QMS. The introduction line (capillary and pin-hole) and the measurement chamber are optimized by the constructor in order to reduce mass segregation problems. The whole device is compact and can be easily moved. It is controlled by a PC using RS232 connection. The acquisition software allows various spectrometer settings and gas intensities acquisition. A calculation of the calibration coefficients can also be performed automatically. However, this function is not used in our case for specific reasons explained later in this paper (see the section about calibration). The aspiration flow-rate of the QMS is about 1 Standard cm<sup>3</sup>/min.

## 3. CALIBRATION PROCEDURES

### 3.1 In the PANDA facility

Calibrating a QMS with air/helium mixtures is quite a standard procedure. In PANDA, gas bottles of mixtures of known compositions can be connected to the QMS via the multi-ports valve (figure 2). Some similar calibration test results will be given for the MISTRA facility. This section will focus on calibrations for which steam is present.

#### 3.1.1 Attempts of calibration tests with mixtures containing water vapor

The initially designed calibration set-up, as shown in figure 2, including a so-called (temperature-controlled) humidifier, which allows one to add steam to air or any calibration gas, was used. Vapor content in the sampled gas was estimated by means of dew-point meter (aluminum oxide humidity probe

from Panametrics) associated with a vacuum gauge (Compact Capacitance Gauge CMR 261 from Pfeiffer Vacuum). The probe gives the Dew-point temperature and the gauge indicates the total pressure at the same location. The vapor content is deduced from these two measurements (and using steam tables). Because these probes cannot withstand much more than normal room temperatures, the pressure in this part of the vacuum system is kept low to avoid condensation ( $P < 23$  mbar at  $20^{\circ}\text{C}$ ) by means of an additional rotary pump (end-vacuum:  $10^{-2}$  mbar).

Unfortunately, this set-up did not allow us to perform successful calibration tests. The difficulty came from the accuracy of the humidity measurement.  $\pm 2^{\circ}\text{C}$  is the accuracy given by the vendor. Such an error can lead to an important uncertainty in the determination of calibration factors. It was realized that the determination of the vapor content in mixtures generated by the humidifier, using a dew-point meter associated with a vacuum gauge was not precise enough to calibrate the QMS. Because of the way the gas samples with water vapor are produced, it was difficult to work in the adequate QMS pressure range and to control the vapor content at the same time. Moreover, the vacuum system configuration used for steam calibrations had to be different from the one to be used in a PANDA test.

### 3.1.2 Tests in a ‘steam test section’

As our attempt to use the designed calibration system was not successful, some tests were performed to test the ability of measuring gas concentrations (steam, air and helium, including high steam partial pressures) in a pressurized vessel (from 1 up to 7 bar). The experimental set-up (figure 3) allows one to mix gases in a vertical cylindrical heated vessel (height: 1m; diameter: 0.15m). The different gases are injected at the top of the vessel, and the mixture permanently exhausted at the bottom. The vessel is supplied by a steam generator and air/helium mixtures are coming from a gas bottle of known composition. An oxygen probe (from Novatech Controls) and a pressure transmitter measuring respectively the oxygen partial pressure and the total pressure are placed in the vessel. Using these measurements and knowing the composition of the dry gas mixture, steam and helium concentrations can then be deduced. These concentrations are compared to the values given by the QMS. We first performed experiments with binary air/steam mixtures and we finally studied helium/air/steam mixtures to estimate the accuracy of QMS measurements.

#### Air/steam mixtures:

Some examples of results are reported in figure 4a where ratios of ion currents are plotted. From this coarse calibration, one can derive a calibration coefficient for steam. Using the same data than those shown in figure 4a, the QMS data (if the derived calibration coefficient is used in the QMS software) are compared with the measurements from the probes in the test section. The following difference has been plotted (figure 4b):

$$E(\%) = 100 (x_{\text{H}_2\text{O\_QMS}} - x_{\text{H}_2\text{O}})$$

Thus, as an order of magnitude, absolute measurement errors could be kept within a  $\pm 4\%$  range for any steam concentration in the vessel. This error appeared to be independent of the steam partial pressure and of total pressure in the vessel.

#### Air/steam/helium mixtures:

Some examples of results with air/steam/helium mixtures are shown in figure 5. The measured ion current ratios  $I_{\text{He}}/I_{\text{N}_2}$  and  $I_{\text{H}_2\text{O}}/I_{\text{N}_2}$  are plotted as a function of measured concentration ratios in the test section. These measurements were carried out by adding steam to a helium/air mixture of known composition (gas bottle). Consequently, each set of measurements corresponds to a constant  $x_{\text{helium}}/x_{\text{air}}$  ratio.



### 3.1.3 Conclusion

The results obtained in the ‘steam test section’ demonstrated that the designed system is able to measure concentrations with an accuracy in the expected range. However, in order to provide a much more complete set of calibration data, an experimental set up enabling us to reproduce calibration routines with less effort and time with various air/steam/helium mixtures is now being developed in PANDA.

## 3.2 In the MISTRA facility

The MISTRA sampler (figure 7) is a complex system with a large number of potential uncertainties on the final measurement. However, it is possible to identify three main categories:

- Uncertainties due to sampling and storage
- Uncertainties due to sample transfer
- Uncertainties due to the analyser

It is very difficult to individually quantify these sources of uncertainty. Nevertheless, we can estimate a global uncertainty for the whole sampling system. This evaluation takes at the same time the sample transfer and the QMS calibration into account. In other words, the whole sampling system (not only the analyser) will be calibrated, and the global corresponding uncertainty will be evaluated.

This assessment of calibration and statistic uncertainties is carried out from standard non-condensable gaseous mixtures. These gas mixtures are connected to three sampling cells of the sampler, and are analysed three by three using the procedure used in a MISTRA typical experiment.

### 3.2.1 Calibration

Calibration presented on figures 9a and 9b are obtained for a specific experiment. In this experiment, we wanted to follow the time evolution of two molar fraction ratios ( $X_{He}/X_{O_2}$  and  $X_{He}/X_{N_2}$ ), during an injection of helium in an air-steam-nitrogen mixture (Magnaud, 2003).

The calibration consists in plotting the linear response of  $I_{He}/I_{N_2}$  versus  $X_{He}/X_{N_2}$ , and of  $I_{He}/I_{O_2}$  versus  $X_{He}/X_{O_2}$  (where  $I_a$  is the measured current for a species, and  $X_a$  its molar concentration). We expect a linear response for those calibrations because of the theory of measurement:

$$P_a = K_a I_a \text{ that implies: } \frac{P_a}{P_b} = \frac{X_a}{X_b} = \frac{K_a I_a}{K_b I_b}$$

With:

- $P_a$  the partial pressure for species a
- $I_a$  the current measured for species a

The mixtures used for this calibration were selected according to the configuration of the experiment. Those calibrations are specific to the awaited ranges of concentrations ratios ( $0 \leq X_{He}/X_{O_2} \leq 4.8$  and  $0 \leq X_{He}/X_{N_2} \leq 1.3$ ).

However, the number of points of calibration has been limited to four different standard gas mixtures (100% air, 5% helium in air, 25% helium in air and 50% helium in air). Obviously, uncertainties of measurement were established consequently. During the experiment, three standard gas mixtures are analysed periodically in order to check the validity of the coefficients of the regression lines.

### 3.2.2 Uncertainties of measurement

The calibration was carried out on an important number of points of measurement (repeatability tests), thus creating a group of several hundreds of points. The first step of the uncertainties study is to confirm that the distribution of  $I_a/I_b$  follows a normal law, thanks to repeatability tests (see figure 10).

This allows the statistic evaluation of the uncertainty of  $X_a/X_b$  measurement, calculated starting from the total variance of  $I_a/I_b$  for a given  $X_a/X_b$ .

This total variance is due to the residual variance  $S_r^2$  increased by the inaccuracy on the determination of the regression line (in our case, the number of measurements is enough to consider that this inaccuracy is negligible compared to the residual variance).

Since the experimental regression is never perfect, fluctuations of  $I_a/I_b$  around the regression line for a given  $X_a/X_b$  still exists. It is then possible to define a residual variance of  $I_a/I_b$  called  $S_r^2$  :

$$S_r^2 = \frac{\sum \left( \left( \frac{I_a}{I_b} \right) - \left( \frac{I_a}{I_b} \right)' \right)^2}{n}$$

with:

- n the number of measurements
- $I_a/I_b$  the experimental value of the currents ratio
- $I_a/I_b'$  the calculated value (thanks to the regression line) of the currents ratio

It finally yields:

- Regression line:

$$\frac{I_a}{I_b} = a \frac{X_a}{X_b} + b$$

- $(X_a/X_b)_0$  value for a measured  $(I_a/I_b)_0$ , and the associated uncertainty :

$$\left( \frac{X_a}{X_b} \right)_0 = \left[ \frac{\left( \frac{I_a}{I_b} \right)_0 - b}{a} \right] \pm \frac{1}{a} \sqrt{S_r^2}$$

These equations allow the calculation of the measurement uncertainty concerning  $X_{He}/X_{O_2}$  and  $X_{He}/X_{N_2}$ , witch is quite good in that case:

- $\pm 1.5\%$  of the measurement range for  $X_{He}/X_{O_2}$
- $\pm 1.6\%$  of the measurement range for  $X_{He}/X_{N_2}$

### 3.3 In the TOSQAN facility

#### 3.3.1 Basics

The calibration equations used to determine the volume fractions  $F_k$  from the measured intensities  $I_k$ , using calibration coefficients  $C_k$ , are as follows:

$$F^1 = \frac{1}{1 + C_1 \frac{I_0}{I_1} + \frac{C_1}{C_2} \frac{I_2}{I_1} + \frac{C_1}{C_3} \frac{I_3}{I_1}}; F^2 = \frac{1}{1 + C_2 \frac{I_0}{I_2} + \frac{C_2}{C_3} \frac{I_3}{I_2} + \frac{C_2}{C_1} \frac{I_1}{I_2}}$$

$$F^3 = \frac{1}{1 + C_3 \frac{I_0}{I_3} + \frac{C_3}{C_2} \frac{I_2}{I_3} + \frac{C_3}{C_1} \frac{I_1}{I_3}}; F^0 = 1 - \sum_{k=1}^3 F_k$$

where  $k=0$  stands for nitrogen,  $k=1$  for oxygen,  $k=2$  for water vapor, and  $k=3$  for helium.

The calibration coefficients  $C_k$  are determined experimentally by different ways as it is presented in figure 13 and described in the next three sections. It has to be emphasized that these coefficients are not

obviously the same if different gas mixtures are used (air-helium, or air-steam-helium, or air-steam).

### **3.3.2 Calibration of air-helium mixtures from calibration bottles**

Like in MISTRA, it consists in injecting into the QMS known mixtures of air and helium at various concentrations. The mixtures are obtained from gas bottles which are directly connected to the QMS capillary inlet. The accuracy obtained is then better than 0.5 % vol.

### **3.3.3 Calibration of air-helium mixtures using the TOSQAN QMS sampling system**

Air-helium mixtures are produced in a small vessel (15 l) to which a standard TOSQAN sampling line is connected (figure 12). The procedure of this test is as follows:

- the small vessel is initially filled with air at ambient pressure and temperature;
- helium is injected from the bottom of the vessel with a quite high velocity, making quite realistic the assumption of homogeneous mixture inside the vessel; however, this homogeneity is not checked and this is the negative point of this calibration method;
- the total pressure increases (the gas temperature also); a constant pressure stage is obtained; it is important to wait some time (1 minute approximately) to reach a constant pressure level, some relaxation of the pressure curve can occur; on the other side, the measurement has to be performed quite fast in order to avoid mass stratification;
- using the ideal gas law, helium volume fraction is calculated from the measured pressure and temperature (assuming saturated conditions);
- sampling is performed inside the vessel (for less than one minute, taking into account the transfer time which is about 10 to 20s); it is assumed that the composition of the mixture is not changed during this sampling;
- a second, third, fourth, etc. injection of helium is performed, leading to new pressure stages and calibration points.

Results are presented in figure 13. The accuracy obtained is about 1 % vol. for the range of volume fraction of interest (helium volume fraction below 30%). For helium volume fractions higher than 50%, a deviation from the calibration curve is observed, probably due to a non-homogeneous helium-air concentration inside the vessel.

### **3.3.4 Calibration of air-helium-steam mixtures using the TOSQAN QMS sampling system**

Steam-air-helium mixtures are produced in the same small vessel as the one used for air-helium mixtures calibration (see figure 12). Different values of steam volume fractions can be obtained by producing steam (water evaporation) and injecting air and helium. The procedure of the test is as follows:

- the vessel is initially at ambient pressure and temperature with a small amount of water at its bottom;
- the vessel walls are heated so that the gas temperature inside the vessel reaches a stable value of 140°C; pressure is increasing, due to temperature increase and water evaporation;
- in order to produce more steam, a thermal resistance heats the water, and evaporation leads to a rapid increase of pressure (0.4bar in less than 200s);
- sampling is then performed during approximately 300s; since during that time, the mixture composition cannot be assumed to be constant an evaporation rate is calculated experimentally; using the pressure increase occurring when the water thermal resistance is switch off and when no sampling occurs (the pressure increase is then only due to steam evaporation);
- the resistance heating the water is switched on three more times, leading to three increases of pressure and thus three different steam concentration levels and three sampling sequences;
- air is injected four times into the vessel, leading to four pressure increases, four more steam

concentration levels and four sampling sequences; the same is performed with helium injections; the calibration curve is obtained from the four steam production stages, four air injection stages and four helium injection stages.

This calibration method is based on several assumptions, the main ones being the gas mixture homogeneity inside the vessel and the experimental evaporation rate. It cannot be considered as a precise calibration method but allows the determination of a set of calibration coefficients for steam-air or steam-air-helium mixtures. Results are presented in figure 14. The steam volume fraction uncertainty is taken as the relative difference between the theoretical mean value and the experimental one. The mean uncertainty found on all the points is 2.7% (2.3% without the calibration point at 80 %vol. which has a high error). However, a great part of this calibration uncertainty is due to the theoretical mean value calculations. The latter are performed using pressure and temperature measurement in the ideal gas law, combined with the evaporation rate calculation. Furthermore, because of water evaporation occurring during the whole test, reducing steam concentration below 40 %vol. is difficult. The steam calibration curve is thus given for volume fractions higher than 40 %vol.. The volume fraction error bars are the dispersion over the mean values obtained with the QMS. Points having an important error correspond to low acquisition times where fluctuations were observed.

The main problem of this calibration is that it is not possible to know in advance the exact concentrations that will be produced. These concentrations are determined by post-processing after the test. For this reason, the option given by the Fabstar software, which consists of an automatic calculation of the calibration coefficients cannot be used, since it is necessary to know in advance the exact concentrations.

#### 4. IMPLEMENTATION IN THE TEST FACILITIES

##### 4.1 Description of the developed gas sampling systems

The three developed systems are multi-points measurement systems. However, they are based on different sampling principles. A basic comparison of their capabilities in terms of number of channels and measurement rates is given in Table 1. Detailed information about the configurations adopted in the three facilities is given in the following sections.

Facility	Number of channels	Time during which each sample is analyzed in the QMS	Time between 2 successive measurements at the same channel	Basic characteristics of the system
PANDA	27	20 sec.	9min	The 27 channels are successively scanned: for each channel, gas is sampled and analyzed in the QMS during 20sec.
MISTRA	54 (2 cycles of 27) 8 (1 cycle of 8)	35 sec 35 sec	45-50 min 8-10 min	2 successive cycles: during each cycle, samples from 27 channels (or less) are simultaneously sampled and successively analyzed
TOSQAN	54	20s to 40s	2-6min	Each channel can be scanned independently and continuously; channels are sampled and analyzed successively; various cycles can be performed

Table 1: Current characteristics of the multi-points systems.

### 4.1.1 In the PANDA facility

The PANDA gas concentration measurement system was designed to provide a time history of the gas concentration at each measurement location. Gas is sampled in the PANDA vessels through capillaries (length: 21m ; inner diameter: 0.80mm). A maximum of 39 channels (capillary inlet ports) is available. The capillaries are connected (via a valve manifold) to a multi-ports valve that continuously and successively scans the different ports corresponding to the measurement locations in the facility according to a programmed sequence. Usually, the last port to be scanned in the sequence is connected to a reference gas mixture: the data from this port will help to appreciate the stability and the response time of the instrument over the test period. The valve and the pressure conditions permit a very fast switching between ports. The configuration of the vacuum system has been especially designed to keep the pressure within the QMS as constant as possible when the different ports are scanned, in order to improve the accuracy of the measurement. A diaphragm pump (low-end vacuum around 80 mbar) is used to exhaust gas samples from all the non-selected ports and to maintain the adequate pressure at the QMS inlet. This pressure is controlled during the test by means of a vacuum gauge.

Concerning the PANDA arrangement, the sampling frequency, i.e. the number of capillaries sampled per minute, is limited by the amount of time the QMS must spend at each port to obtain a proper measurement. The response time of the system is directly related to the time needed for a gas sample to totally replace the previous one in the analyzer. Because of steam properties, the worst case typically corresponds to the transition between a port to which pure steam is sampled and a port supplied with a dry gas. For example, a sampling time of 20 sec. spent at each port was chosen for the last PANDA test series. Because of the chosen measurement options, the actual QMS measurement rate is about 1Hz, i.e. a new set of QMS data (3 gas concentrations) is available very second. As the QMS was programmed so as to stay 20 sec at each port before switching to the next port, it means that about 20 records are available for each sampling period at a given port. Because of the limited response time of the system, we have considered for these tests that it was necessary to wait 15sec. to get a proper measurement. Only the data acquired 15 sec. after the first record of this sampling period are used. These data from the last records are averaged and only one mean time and one set of gas concentrations is conserved. As 27 capillaries were used, this means that at each measurement location one new measurement (consisting of three molar fraction values for the three gas species i.e. air, steam and helium) is available every 540s (9 minutes).

The choice of this sampling time is of course a trade-off. In many situations, it appeared this time could be much further reduced (between 5 and 10 sec spent at each port seems to be feasible). To summarize, this choice has to be optimized according to the experiment to be performed.

Some advantages of using capillaries are obvious. The sampling probe (i.e. the tip of a fine capillary tube) is not cumbersome and can be installed exactly at the desired location in the vessel gas spaces. A special support was designed to fix a thermocouple at only 3.5 millimeters distance from the gas sampling location. Moreover, even if some effort is required, it is always feasible to move the capillaries and fix them at a different measurement location for a particular experimental campaign, if one has a lot of interest, for example in getting more refined information about gas distribution in some specific regions. Each capillary has an area reduction at the tip (where gas is sampled) to produce a pressure loss that prevents steam condensation along the length of the capillary that is within the pressure vessel. Different tests have been carried out to choose the optimal capillary tip reduction to be used (Auban, 2001). A tip reduction consisting in reducing the outer diameter to 0.75mm over a 50mm length has been chosen for each capillary installed in PANDA. This choice appeared to be a good trade-off between low gas consumption and acceptable QMS response time.

Different heating systems were installed to avoid any problem due to steam condensation inside the sampling line especially when nearly pure steam is present. The entire path of the gas sample from the vessel to the QMS is heated. Capillaries issuing from the same flange are grouped, heated and installed in teflon tubes that serves as a rough insulation up to the valve manifold. All the valves (enabling to isolate the QMS set-up from the gas samples coming from the vessel through the capillaries) have been installed in a heated box. From this box to the multi-ports valve, capillaries are also grouped, heated and insulated with an auxiliary heating system. The multi-ports valve itself is also heated and temperature controlled

(max. 120°C). A heated insulated box covering the valve and the exhaust lines to the diaphragm pump has been designed and constructed. It was checked that enough heat is supplied to the sampling lines by the different heating systems to avoid any condensation problem and to maintain the quality of the QMS signal (no very large and sudden fluctuations, peaks,...etc) for any condition in the vessel.

#### 4.1.2 In the MISTRA facility

The gas analysis system must allow, at a given moment, the establishment of the cartography of the different species inside the enclosure. That implies to have a significant number of measurement locations - 54 - distributed in the experimental volume (100 cubic meters). It is also required to know the gaseous composition at the different measurements locations at the same time. Finally, we must follow the time evolution of the gas concentration of a reduced number of samples, for example during transient helium injections. In order to fulfil these criteria, the experimental approach is based on two essential principles, namely:

- *In-situ* sampling of the gas at all the different measurement locations at the same time
- Sequential analysis of the gas composition

This approach led to the design of a gas sampling system (called “sampler”, see figure 7), for sampling and storage of gas from the different measurement locations, and an analysis line by mass spectrometry for the quantification of gas composition. A specific processing system has been developed for the data management of the sampler.

The experimental process is characterized by three main steps, namely sampling and storage, transfer of the sample and analysis by QMS (figure 8).

##### Sampling and storage

The sampler is made up of 30 sampling cells that allow the storage of the gas (27 are dedicated to the samples from MISTRA containment, and three to the sample of standard gas mixtures). So, the 54 measurement locations are analysed sequentially (27 during a first sampling and analysis cycle, and the other twenty seven during a second cycle).

The sampling step needs the sampler to be conditioned. Before sampling gas at the different locations, we must indeed obtain a sufficiently low residual pressure inside the cells and the lines (about 1mbar absolute). The gas previously analyzed is thus pumped out of the sampler. The created depression allows the sampling of new gas by simply opening the electro-valve.

After this step, called “draining”, the next operation is a rinsing. The aim of this step is to eliminate the gas accumulated (after the last sampling) upstream from the electro-valves, since this gas is not representative of the gas to be analyzed.

Finally, another draining is realized to prepare the system before sampling the new samples to be analyzed.

The next step is the storage of the gas samples. When a cell is filled, the electro-valve that ensures the filling is simply closed, so that the sample is insulated before its transfer and analysis. The sampling and storage step is then over, and the absolute pressure inside the sampling cells is about 700mbar. This pressure level influences the speed of the system: the lower it is, the shorter the time needed to fill the cells but the longer the time to fill the buffer capacity.

Because of the presence of steam, the speed of the system is mainly limited by the time needed to drain the buffer capacity. This speed may be increased by heating this capacity up to 150°C (instead of approximately 100°C) in order to reduce adsorption effects and by improving the pumping system.

It's important to note that the pressure in the whole sampler is always under 1 bar absolute, and that it is entirely heated. Those precautions have been taken to prevent condensation in the sampler, since the mixtures to analyse can contain up to 70% vol. of water vapor.

Concerning the main dimensions characterizing the system:

- The internal diameter of the sampling lines is 1mm, and the length is between 2 and 13 meters. This dimensioning results from a compromise between the pressure loss and the segregation effects.
- The choice of the volume of the sampling cells (200cm<sup>3</sup>) is also a compromise. On the one hand, the sample must flow in the QMS for a duration that is longer than the response time of the instrument. On the other hand the total volume taken in MISTRA containment during the sampling step should not affect too much the test conditions.
- The duration of the sampling step (opening of the electro-valves) depends on the MISTRA pressure (about six seconds for a total pressure of 3 bar absolute, and three seconds for 5 bar absolute)
- The storage period depends on the number of samples to analyse. For example, for an 8-samples analysis, this time is about 8-10 minutes, and 20-25 minutes for a whole cycle (27 analyses). This point is very important if leakage occurs, since the shorter the time of storage is, the less the effects of leaks are prejudicial.
- The whole sampler is heated (between 100 and 120°C) in order to prevent steam condensation.

#### Transfer of the sample to the analyser:

All the cells are linked to a gas collector, which leads the gas from the cells to a buffer volume, and then to the analyser. The gas collector and the buffer volume are heated. The buffer volume (2 litres) is very important as it enables to have a sufficient mass of gas within a large volume at low pressure (about 5mbar absolute). That ensures the mass spectrometer response to be stable with time, since the consumed gas flow rate is low compared to the buffer volume capacity.

The transfer process is very similar to the sampling and storage ones. The first step is a draining of the collector and buffer volume, thus the necessary depression is created to fill the buffer. Then, a rinsing step occurs before another draining. The gas previously analysed is thus exhausted.

After those operations, the buffer is filled up to 5mbar absolute through the electro-valve located downstream the cell containing the sample to be analysed.

The design of the different elements of the sampler, preventing condensation and segregation to occur, ensures that the gas going to the analyser is representative of the gas in the MISTRA containment.

#### **4.1.3 In the TOSQAN facility**

The TOSQAN sampling system is presented in figure 12. It consists of 9 heated lines, each one connected via a rotating valve to 6 fine tubes. The latter are fixed on a steel rod and penetrate into the TOSQAN vessel. 54 gas sampling points are thus obtained, located at different heights and radii. Mass stratification and horizontal profiles inside and near the walls can be measured. Sampling is performed using a continuous pumping inside TOSQAN and re-injecting the gas mixture on the bottom of the vessel through a ceramic filter in order to diffuse at very low velocity the gas mixture (minimizing flow perturbation inside the vessel). The QMS capillary is connected to this sampling circuit. The facility is also designed to perform static sampling (i. e. to pump with the QMS the gaseous mixture sampled in a small capacity, whereas for continuous sampling, the gaseous mixture is circulating in a line coming from and going to the TOSQAN vessel), however, tests have shown better and easier improvement for the continuous sampling: static sampling implies to work higher than the atmospheric pressure, since in case of small leaks, ambient air can enter the sampling lines, modifying the gas composition; furthermore, static sampling presents very slow transfer times.

#### Verifications before each measurement:

Before each TOSQAN test, the air concentration in the TOSQAN experimentation hall is checked. Calibration of helium-air mixtures from calibration bottles is also checked regularly. However, since

steam-air-helium mixture calibrations are quite long and more demanding calibration procedures, they are only performed if an important change in the QMS or the sampling system occurs (filament change for example).

#### Acquisition times:

Each measurement has two characteristic times. The first one is an acquisition time of the mass spectrometer (20s to 40s depending on the measurement to be performed): it is the time needed by the mass spectrometer to scan all masses and to 'find' which masses are present in the gaseous mixture. It has been observed that this acquisition time, called "dwell time", is of particular importance to perform good measurement. Secondly, the integration time, i.e. the time during the sample is collected is generally between 120 s and 360 s (also depending on the kind of test or measurement). Mean values of the volume fractions with their standard deviation (divided by the root square of the number of measurement points) are calculated. The error bars presented in this paper are given for a confidence interval of 95 %. Note that the uncertainty on the calibration coefficient is not included in this error bar.

### **4-2 Difficulties inherent in the developed gas sampling systems**

The way the gas sampling systems are designed induces some difficulties or uncertainties on the measurement. The examples presented in the following section are taken from the measurement system developed in the PANDA facility.

#### **4.2.1 Gas consumption of the sampling system**

The gas concentration measurement system as it is designed in PANDA requires continuous sampling gas through all the capillaries. Gas is therefore continuously removed from the PANDA facility during the experiment, causing a non-wanted decrease in the facility pressure. Hence, some tests were performed to estimate the overall gas consumption of the gas concentration measurement system (Auban, 2001). These tests consisted in filling a vessel with gas and measuring the gas leak through a capillary similar to those used in the sampling system. The order of magnitude of the flow rate corresponding to 40 capillaries was found to be around a few kmol/day. These results and some coarse assessments proved the relatively low impact of the gas concentration measurement on a PANDA experiment (overall system pressure). Anyway, the importance of this continuous gas removal has always to be considered and discussed.

#### **4.2.2 Uncertainty on the sampling time**

The time at which one given sample is analyzed in the QMS is not the time at which it was sampled in the vessel. The time a gas sample needs to travel should be taken into account when looking at the data. If all the sampling lines are similar, this time mainly depends on the concentration of the transported sample and the pressure conditions. In PANDA, this transit time could only be assessed using pure helium and the vessel being at atmospheric pressure (about 10 seconds). Of course, if one wishes to measure in the course of relatively fast transients, this uncertainty must be seriously considered and this problem would require further investigation.

### **5. VALIDATION OF THE TECHNIQUE USING RECENTLY ACQUIRED TEST RESULTS**

Some examples of results acquired in the test facilities will be presented hereafter. As mentioned before, because it is difficult to calibrate at exactly the same conditions as during a real test, the assessment of the actual accuracy of the measurement remains delicate. Hence, the following results can be considered as a validation of the complete measurement set-up and give relevant information about the



present possibilities and achievements of the technique.

## 5.1 Results in the PANDA facility

These results are taken from some tests performed in the frame of the `TEMPEST` project (Auban, 2003). The measurements point out some stratification phenomena resulting from the buoyant flows generated by helium injection. The resulting concentration pictures of the flow show how helium is being distributed in the vessels during the helium injection phase, and how helium is retained or vented out of these vessels as the injection is stopped.

The QMS provided a time history of the gas molar fractions at each of the 27 measurement locations. At each location, one new measurement is available every 540s. It should be emphasized that a temperature measurement was available in the vicinity of each of the gas concentration measurement locations. In other words, a thermocouple was installed very close (typically a few millimeters) to each of the capillary tips from which the gas was sampled. The presented case refers to the measurements performed in one of the two Drywell(DW) volumes (each volume: 90m<sup>3</sup>) of the PANDA facility.

### Principle of the validation

The present attempt to validate the technique is based on a comparison with data obtained from others sensors. As mentioned above, temperature measurements have been acquired in the vicinity of each gas sampling location. A measurement of the (total) pressure is also available in each vessel of the facility. Moreover, in the DW vessels, some Zirconia (solid reference) oxygen probes have been measuring air partial pressures over the whole test period. Such sensors function properly in relatively low air partial pressure conditions. Thus, in these DW vessels, considering that in this kind of test 0.05bar is the maximum possible air partial pressure, a reliable and accurate information about air fraction was always available.

The time plots of air, steam and helium molar fractions measured by the QMS are shown (figure 6). This set of measurements are compared to data curves (referred as 'COMP' on the legends of figure 6) processed as follows:

\* The air partial pressure is assessed from oxygen probes data and the measurement of total pressure in the vessel allows to derive a volume fraction. By considering the air behaves like an ideal gas, this volume fraction is equivalent to a molar fraction to be compared with the QMS results.

\*Steam is assumed to be at saturation. Some spline interpolation from the steam tables was used to derive the steam partial pressure from the temperature measurements acquired in the vicinity of the gas sampling location. Again, the measurement of total pressure in the vessel allows to derive a volume fraction, which has to be considered as equivalent to a molar fraction.

\*An helium fraction is only deduced by subtracting the two previously processed fractions from one.

### Results

We are looking at the data acquired at only one location in the middle of the vessel. The comparison of the QMS data with the molar steam fraction derived from TC measurement (assuming saturation) is shown on figure 6b. In the early phase of the test just before helium injection, assuming to be very close to saturation is reasonable; hence, an offset (+0.5°C) was applied on the temperature used for the data comparison, so as to get, after this tuning, the derived molar fraction (thick-line curve on figure 6b) close to the QMS molar fractions.

During helium injection, the QMS data seem to show fractions slightly lower, tending to prove that steam is superheated. This observation is in good agreement with the physical phenomena occurring in the vessel i.e. some continuous helium injection in pure steam. The comparison remains very satisfying as helium injection is stopped: the two curves seem to prove that conditions very close to saturation are again established in the vessel.

Figure 6a proves that the QMS technique is also able to follow very small changes in air concentration detected by the oxygen probes.

## 5.2 Results in the MISTRA facility

The results presented here are taken from a particular test performed in MISTRA. The purpose was to study the dilution of helium in an air/steam mixture beforehand inerted with nitrogen. The test can be divided in three parts: first, the air/nitrogen/steam mixture reaches a steady state due to the equilibrium between the injection of steam (which is constant) and its condensation on the three condensers. Then, helium is injected (the injection of steam still operates). Finally, the injection of helium is stopped, and a second steady state is reached.

For this test a particular attention was paid to the measurement of the dilution ratio, that is to say the ratio between the molar fraction of helium  $X_{\text{He}}$  and the molar fraction of nitrogen  $X_{\text{N}_2}$ . The measurements were reduced to eight samples, so that the time between two analyses of the same sample was about 470 seconds.

### Principle of the validation

The validation of the measurement technique is based on the comparison with the results obtained thanks to other sensors (temperature and pressure measurements), and with the knowledge of the initial mass of air, and injected mass of nitrogen. Each one of the sampling lines is equipped with a thermocouple, so that the temperature of the gas sampled is always known. On top of that, a pressure gauge gives the total pressure in MISTRA in real time. Thanks to these measurements, it is possible to evaluate the partial pressure of helium in MISTRA during and after the injection.

It is also possible to evaluate the partial pressure of nitrogen by means of the temperature measurements, the initial mass of air and the injected mass of nitrogen (considering that nitrogen is a perfect gas).

We obtain an evaluation of the dilution ratio simply by division of these two partial pressures ( $X_{\text{He}}/X_{\text{N}_2}^{\text{eval}}$  in figure 11a).

### Results

The results presented in figure 11 are obtained for a sample located at middle height and middle radius in the vessel. In figure 11a, the experimental points are presented with their associated uncertainty ( $X_{\text{He}}/X_{\text{N}_2}^{\text{mes}}$ ), and the evaluation ( $X_{\text{He}}/X_{\text{N}_2}^{\text{eval}}$ ) is superimposed.

It is clear that the evaluation of the concentrations ratio is always inside the limits defined by the uncertainty of measurements, which is very satisfying.

In figure 11b is plotted the relative variation between the evaluation and the measurement, which is obviously greater when the values are small. It is very interesting to note that in the second steady state (after the end of the helium injection), the relative variation between measurement and evaluation is less than 2%.

## 5.3 Results in the TOSQAN facility

### 5.3.1 Stability of the measurements in a steady-state test in the TOSQAN facility

The condensation tests in the TOSQAN facility consist in injecting steam in air in a closed vessel. Pressure is then increasing and reaches a constant value when equilibrium between the injection flow-rate and the condensation flow-rate (filmwise condensation occurs on part of the TOSQAN walls) is obtained. During this so-called steady-state, all other variables are supposed to reach a constant value. Stability of steam volume fraction measurements can thus be checked during this steady-state. Examples are given in figure 15 (the error bars correspond to the standard deviation of the volume fraction measured during the sampling period).

### 5.3.2 Repeatability in a steady-state test in the TOSQAN facility

Repeatability can be checked in two different ways: during the steady-state of a TOSQAN test and for the same test performed on different days.

- During a test, a horizontal concentration profile at the same height can be performed twice. This concerns more the repeatability or the stability of the concentrations during the considered steady-state. Results show a good repeatability (figure 16) where a half profile upon the injection pipe is given. The higher concentration due to the steam jet presence is seen on both profiles.
- A horizontal concentration profile at the same height can be performed during two different days of test. This includes not only the repeatability of the QMS measurement but also the repeatability of the test itself. To check this latter point, it is necessary to calculate by mass balance the mean volume fraction of steam for each of the test since it can differ of 1% vol. or 2 % vol. between the different days of tests (since the air quantity initially inside the vessel is never exactly the same, the injection flow-rate or leak flow-rates can vary from one day to another, etc.). Interpretation of this kind of ‘global repeatability’ study is not obvious, but it can be seen in figures 17 that this repeatability is quite good.

## 6. CONCLUSIONS AND PERSPECTIVES

In the three facilities, some big steps have been made concerning the implementation of the technique. The sampling systems are working correctly providing QMS signals of good quality. Problems related to the pressure in the vessels, the presence of steam or the large scale of the test facility seem to be under control. It is obvious that the main future work concerns calibration and accuracy assessment. The progression of this calibration work with trial and error has revealed the difficulty to work with steam.

### In the PANDA facility:

The procedures initially planned for calibration are not optimal and appears to be very time-consuming. They could not be quickly repeated as a routine work preceding any new experiment in PANDA. The whole range of gas composition in which we were interested could not be covered. Up to now, before each PANDA test, only a calibration with dry gas mixtures could be carried out.

The future work will mainly concern the implementation a new system enabling the generation of calibration gases (Air/steam/helium), the idea still being as close as possible than the normal operation conditions. This system, mainly based on a product from Bronkhorst known as “Controlled Evaporation and Mixing” (C.E.M.), has already successfully been used at IRSN for the calibration of a Mass Spectrometer system in presence of steam (Duriez, 2001). The basic idea of this vapour delivery system is quite simple: water is controlled in its natural liquid state at ambient conditions and consequently evaporated in a continuous way with the aid of the dry carrier gas. At room temperature the liquid (water) is drawn from a container and measured by a liquid mass flow meter. The carrier gas flows (pure air and pure helium) are also measured by mass flow controllers. The three ‘components’ (liquid flow and carrier gas (air/helium)) are mixed by means of special mixing valve and the formed mixture is subsequently led into an especially designed evaporator to achieve total evaporation. The main interesting feature is that there is no need to measure vapor content itself anymore. So, the ability to produce in a shorter time well-controlled and reproducible mixtures over a wide range of composition is expected from this new system. Even if it necessary to have a more refined calibration procedure to get more confidence in the data, the first results acquired with the QMS technique in the course of PANDA tests are quite promising. The QMS results showed a good agreement with the others sensors and a good accuracy has already been achieved over a wide range of molar fractions. The developed system is now part of PANDA instrumentation and will be used in the next experimental programme (Yadigaroglu, 2002). The challenges will be to measure in faster transients and to get sufficiently accurate results to catch the stratification patterns characterized by very low concentration differences in the large vessels.

#### In the MISTRA facility:

The current efforts relate to the realization of a small calibration vessel to improve the current calibration methodology. This device will allow the creation of mixtures of steam and non-condensable gases, such as nitrogen, air and helium for example, with a good accuracy (as good as the standard non-condensable gases mixtures). It will be then possible to make all gas mixtures of interest within a pre-set measurement range. A special system to prevent any stratification in the vessel is developed. The objective is obviously to improve the quality of our calibrations, thus reducing the measurement uncertainty. The system will be applied to the future MISTRA tests (off-centred injection and compartments), to be carried out over the period 2003 to 2006.

#### In the TOSQAN facility:

For the TOSQAN project, a small vessel has been used to produce controlled steam concentrations. First calibrations were performed without steam in order to verify the good mixing in our calibration chamber. The accuracy found in this calibration chamber was lower than the one obtained by gas bottles, but was still sufficient. Steam-air-helium calibrations have then been performed in this vessel, and a procedure has been found to produce the gas mixtures. Results allowed the determination of calibration coefficients that have been used successfully for steam concentration measurements during TOSQAN condensation tests (experimental programs performed for code validation purposes, see Vendel, 2003 and Cornet, 2002). It has been observed that our system does not need frequent calibration, which is a very positive result. Results on TOSQAN tests have also shown the good stability of the concentration measurements. Mass spectrometry in TOSQAN can be improved by reducing uncertainties related to the production of steam and its measurement (better homogeneity inside the calibration vessel). QMS validation can also be performed by comparing the results with other concentration measurements. Further tests will be performed with saturated steam produced in the TOSQAN vessel and using the spray system installed in the facility.

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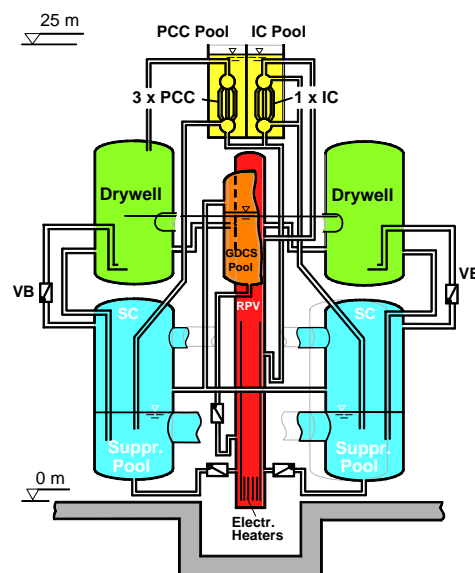


Figure 1: Simplified sketch of the PANDA facility

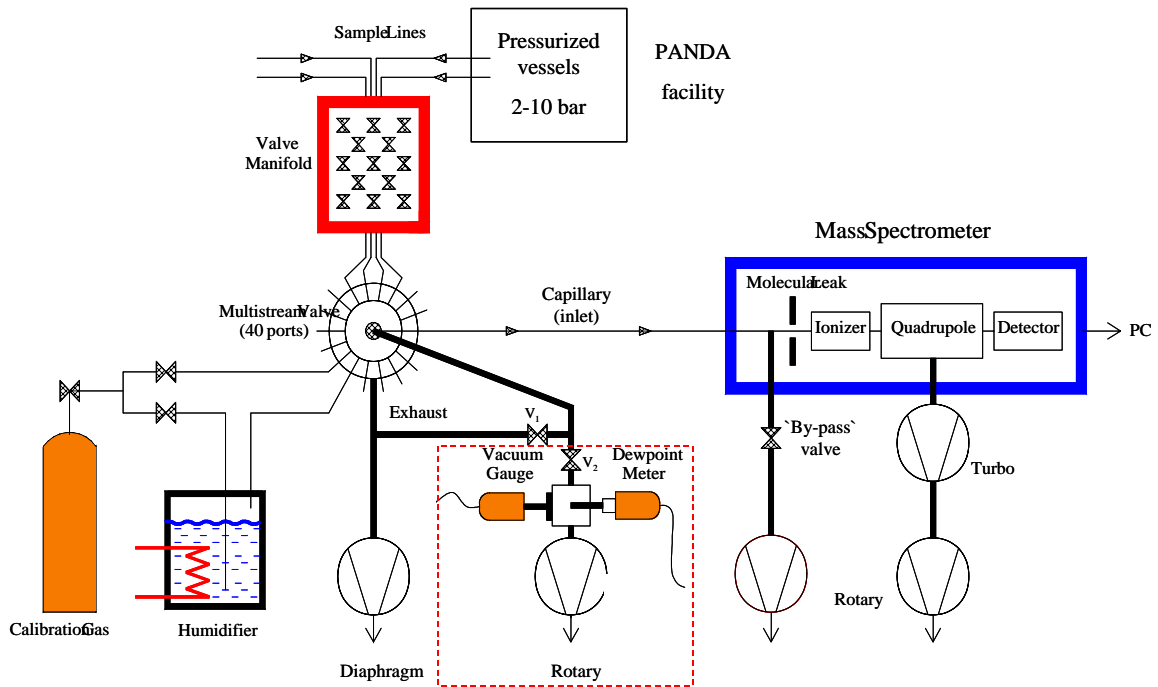


Figure 2: Overview of the gas concentration measurement system in PANDA (The valve ‘V<sub>2</sub>’ was only open for calibration with water vapour (for which the specific part of the system that is surrounded by a red dashed line was used))

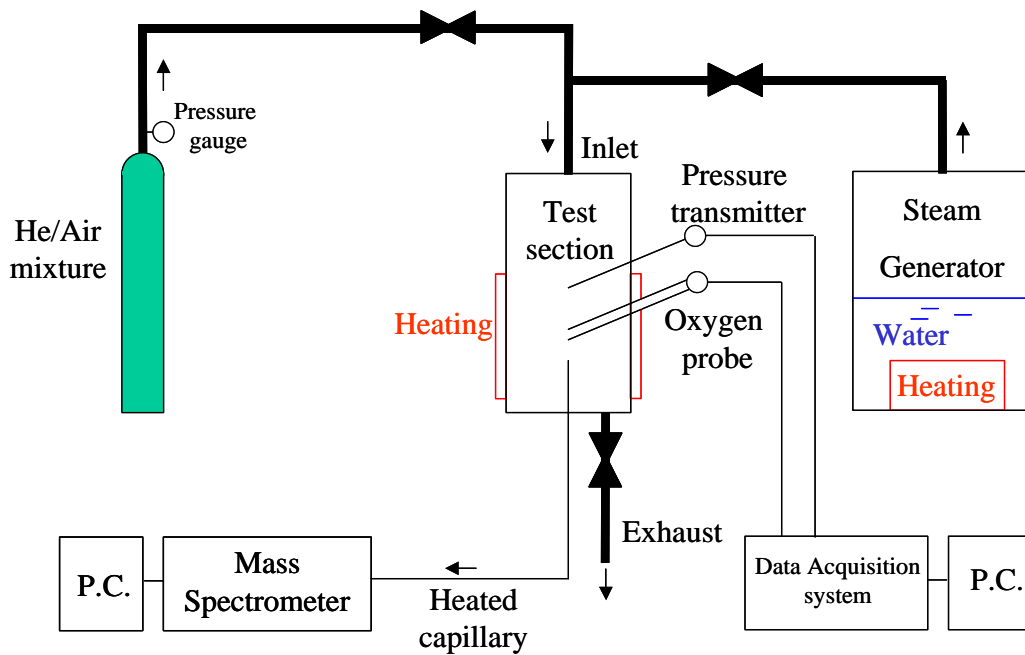


Figure 3: PANDA ‘Steam test section’: experimental set-up

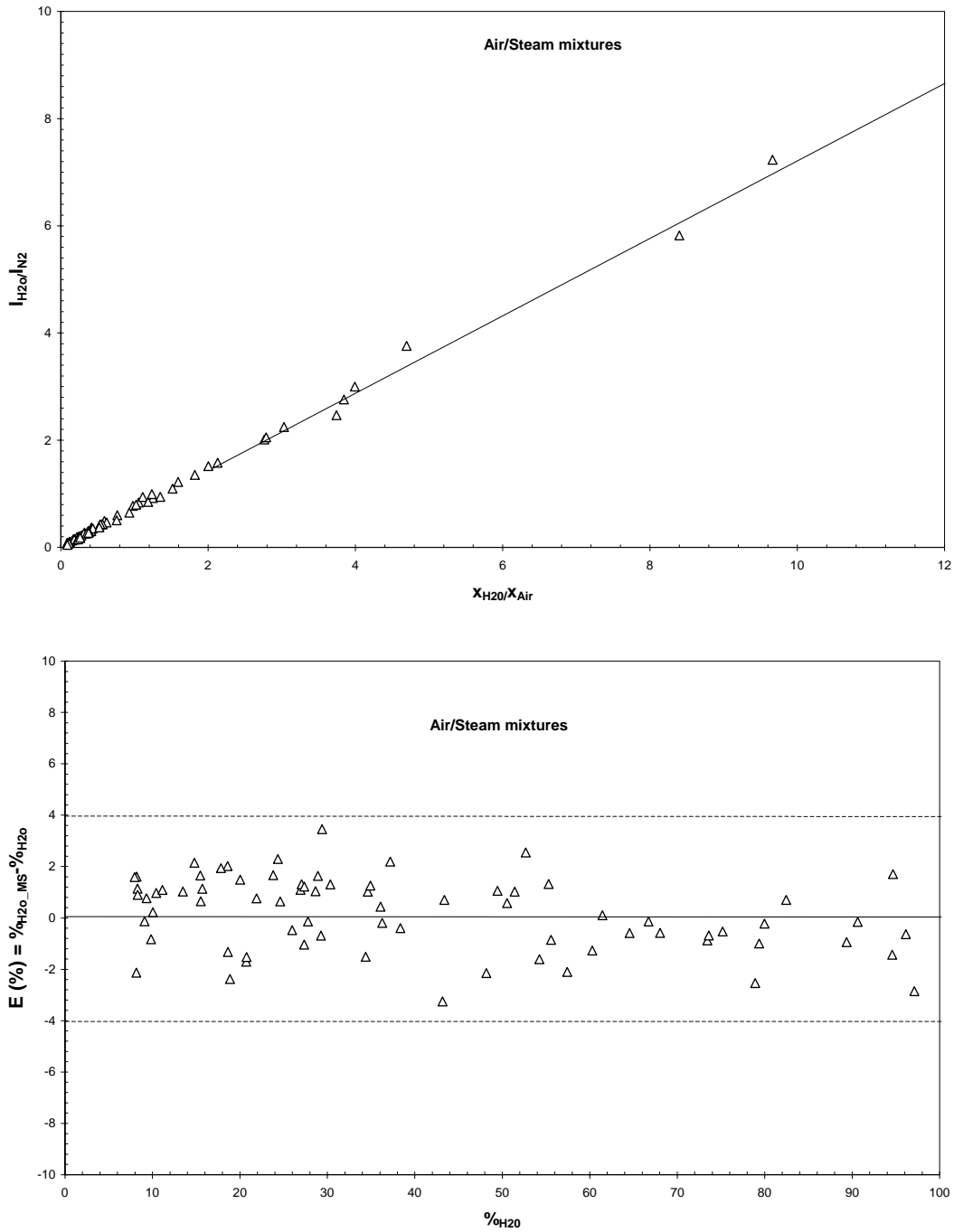


Figure 4: Examples of results obtained in PANDA in the ‘steam test section’:  $x_{Air}$  is derived from oxygen probe measurement,  $x_{H_2O}$  is deduced from total pressure measurement ; (a) (top): water to nitrogen ion current ratios; (b) (bottom): derived absolute error on the water vapour content

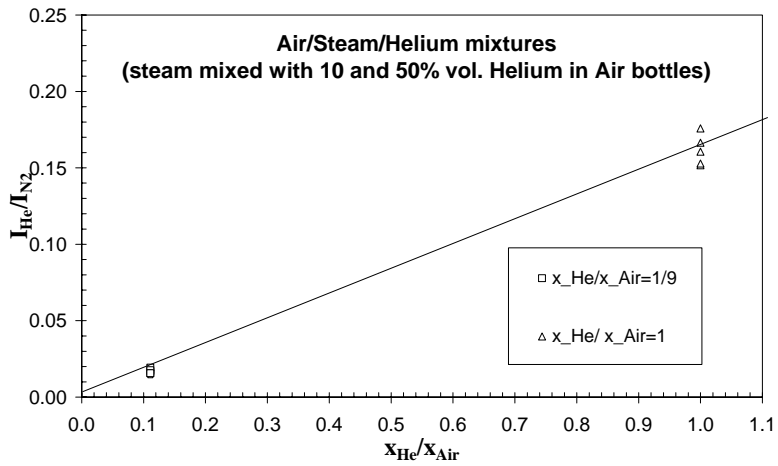
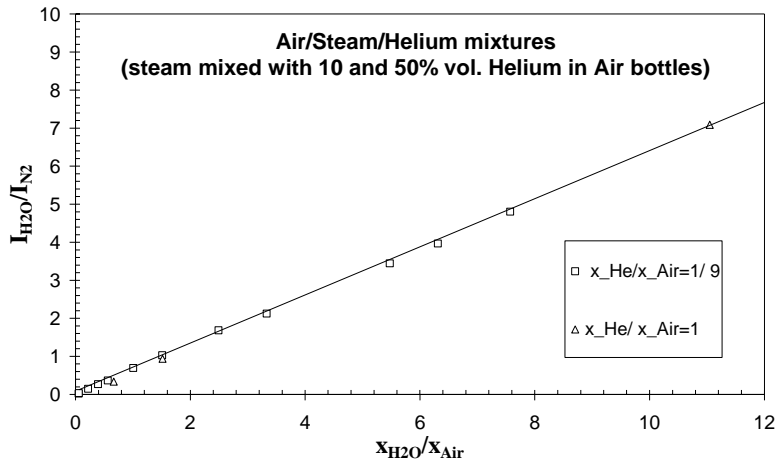


Figure 5. Examples of results obtained in the PANDA “steam test section”: the vessel was supplied with steam from the steam generator and with two different dry gas bottled mixtures;  $x_{Air}$  is derived from oxygen probe measurement,  $x_{H_2O}$  is deduced from total pressure measurement. (a) (top): water to nitrogen ion current ratios; (b) (bottom): helium to nitrogen ion current ratios.



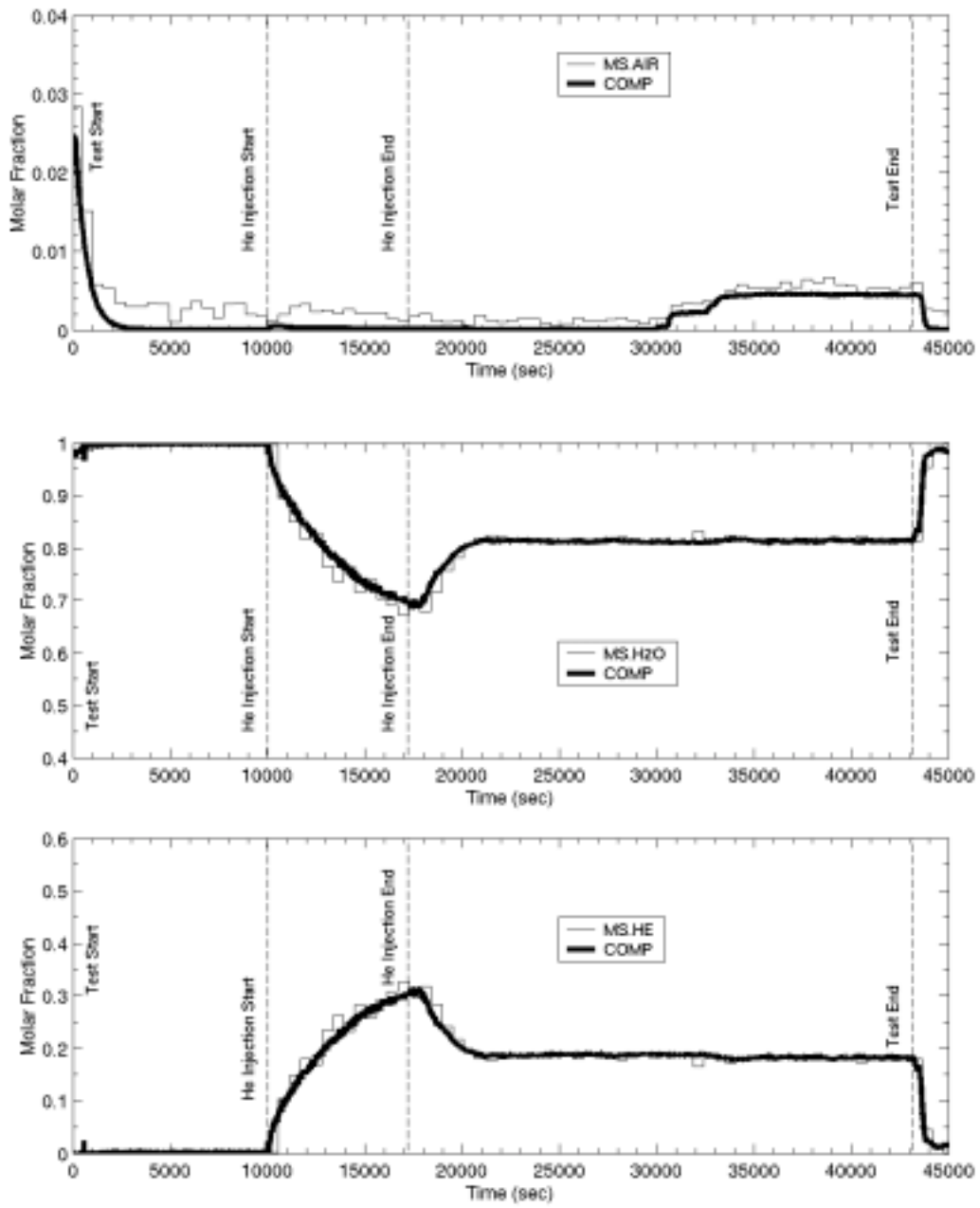


Figure 6. Time history of gas fractions measured in a PANDA test  
 (a) (top): Air; (b) (middle): steam; (c) (bottom): helium..

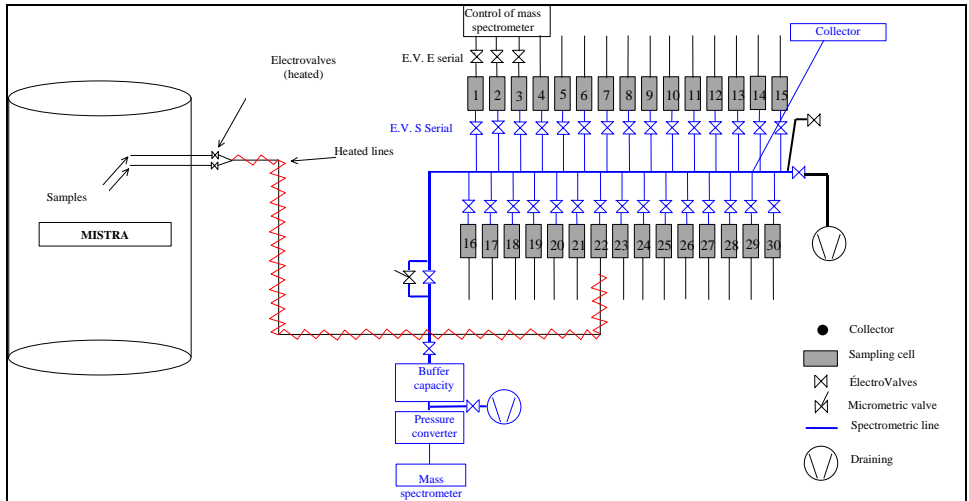


Figure 7: General diagram of the gas Sampling system in MISTRA

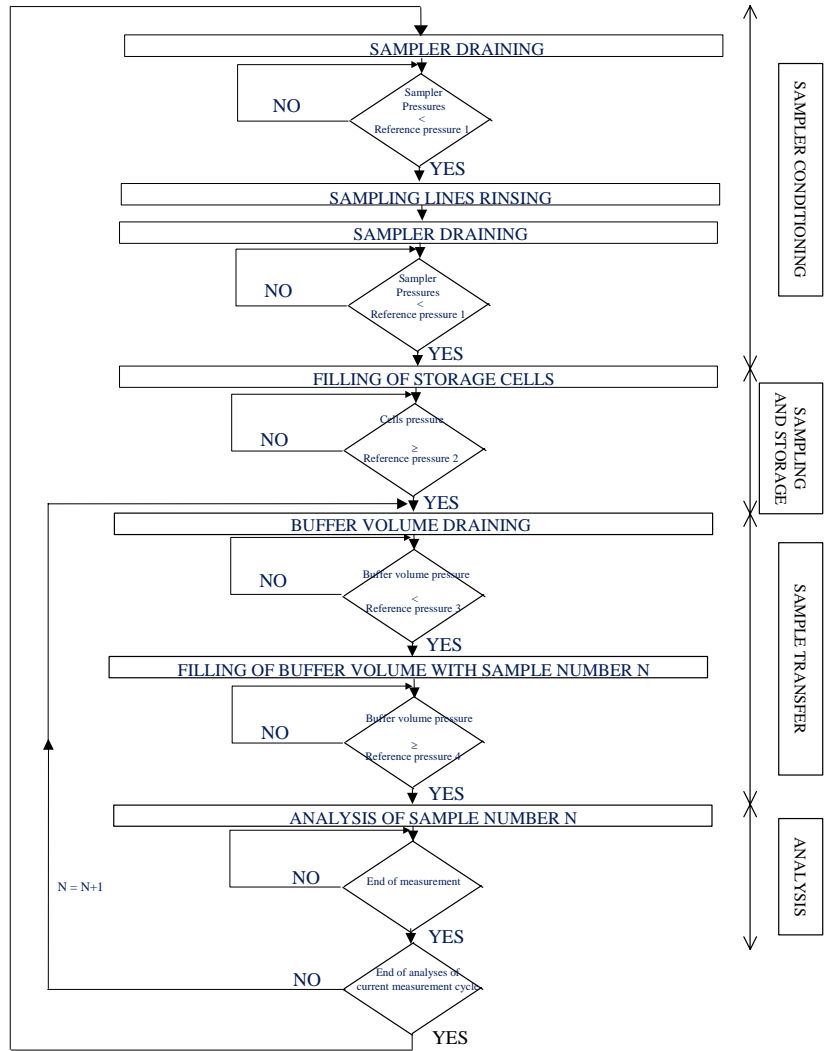


Figure 8: MISTRA facility: sampler management algorithm

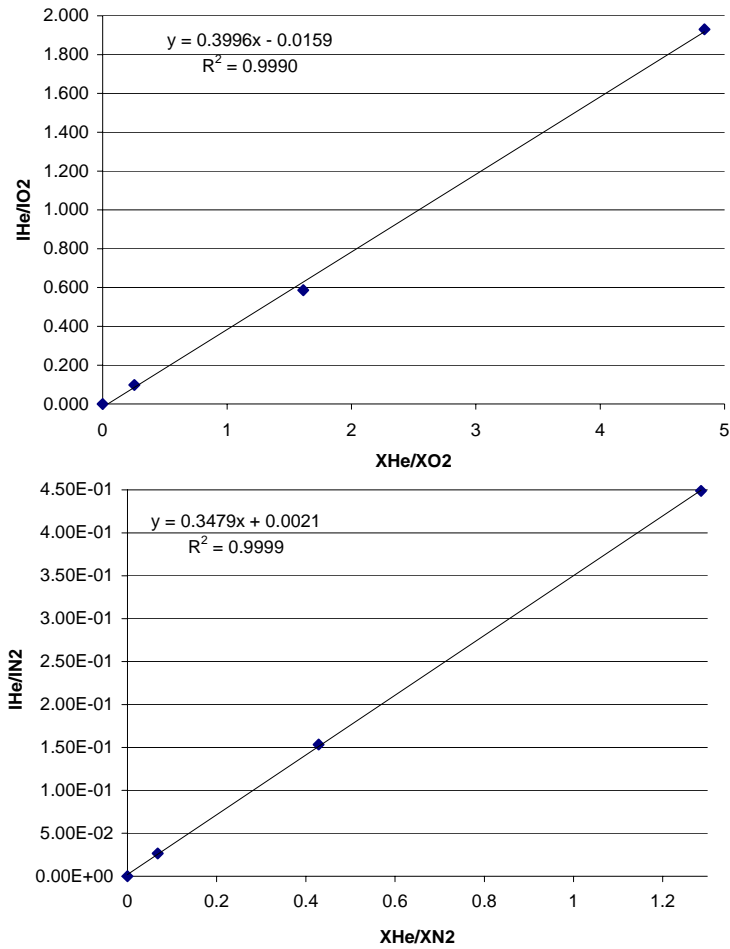


Figure 9: Calibration in MISTRA: a)(top) helium to oxygen ion current ratios ) (bottom) helium to nitrogen ion current ratios

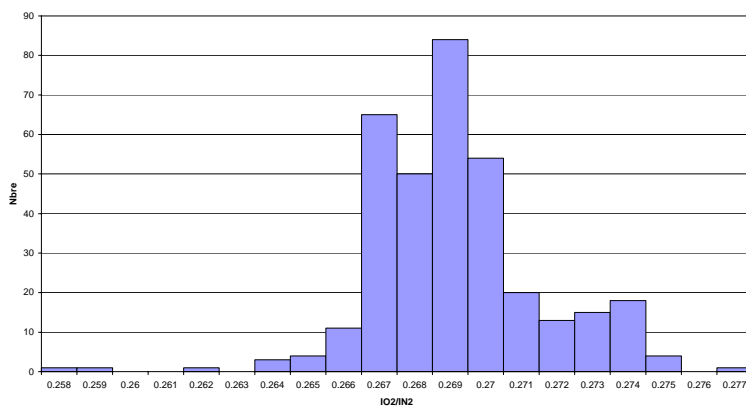


Figure 10. Distribution of  $I_a/I_b$  follows a normal law during a repeatability test (calibration in MISTRA)

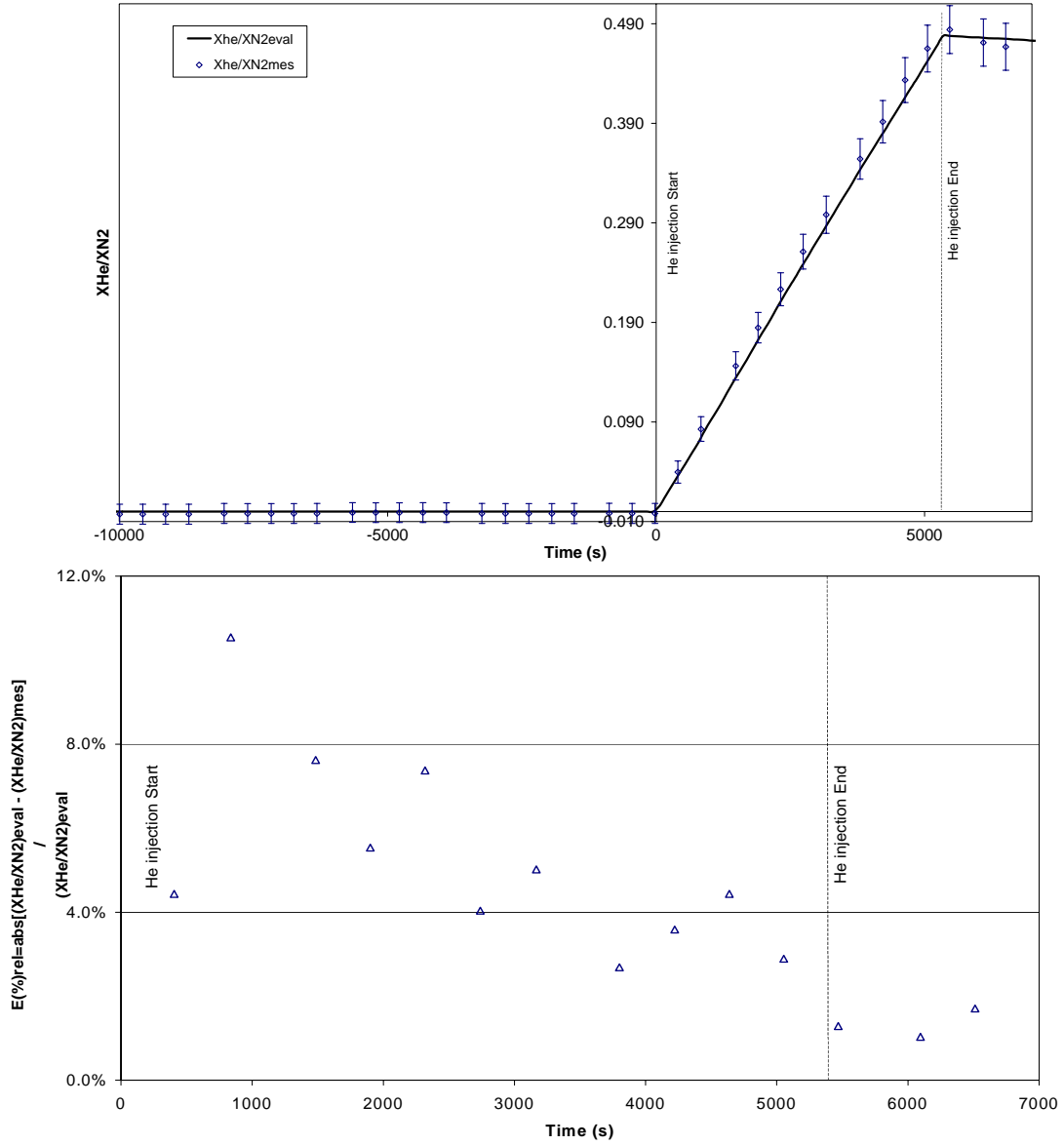


Figure 11: MISTRA experiment: comparison between measurement ( $X_{He}/X_{N2}^{mes}$ ) and estimation by means of pressure and nitrogen injected mass ( $X_{He}/X_{N2}^{eval}$ ) (a) (top). Relative variation between the two methods (b) (bottom) during helium injection and after.

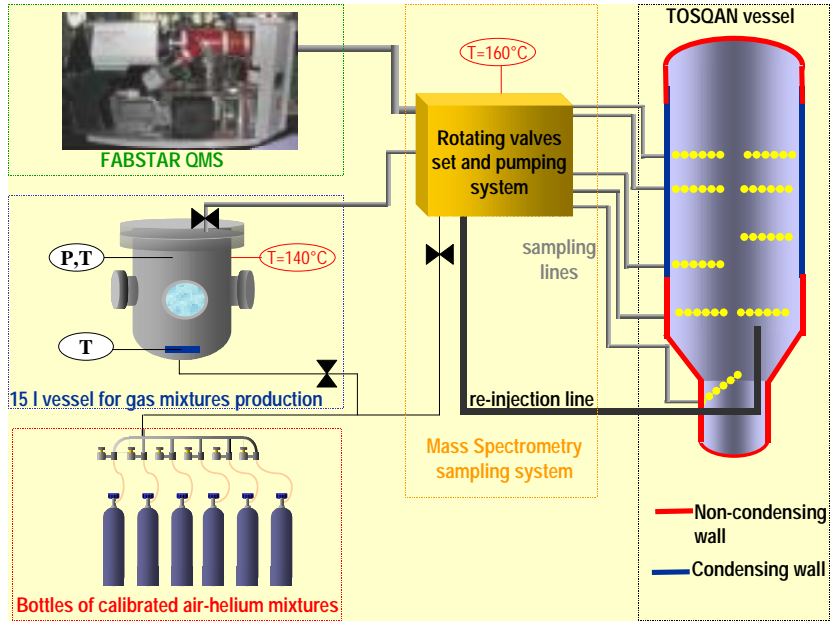


Figure 12: Mass spectrometry in TOSQAN

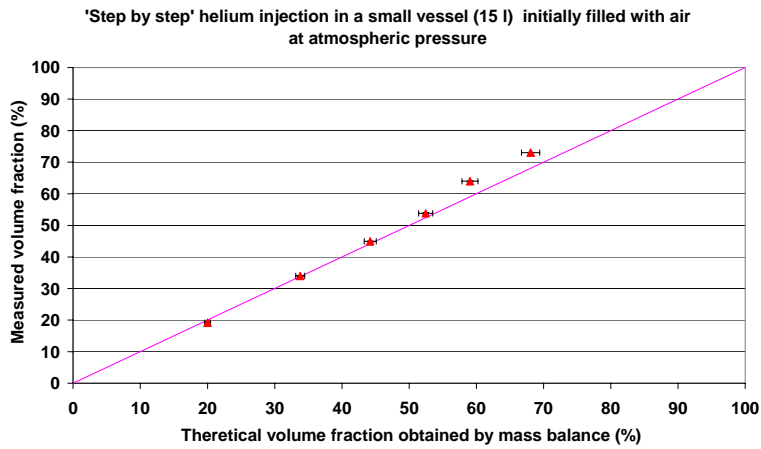


Figure 13: Calibration of the TOSQAN QMS using air-helium mixture produced in a small vessel.

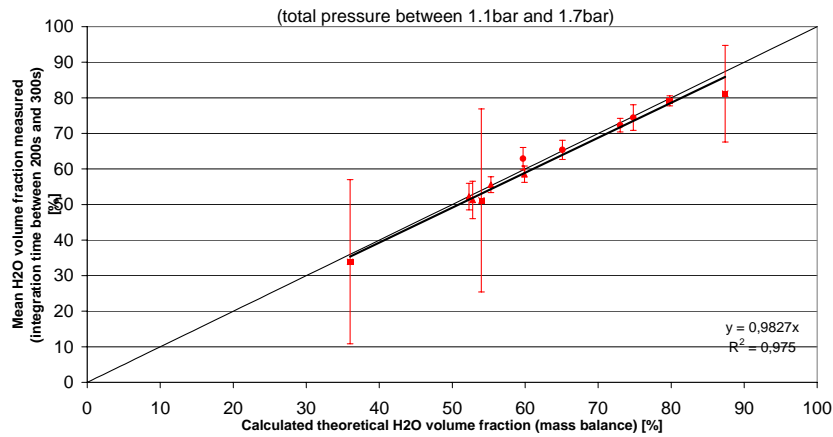


Figure 14: Calibration of the TOSQAN mass spectrometer in a small vessel with air-steam-helium mixtures: H<sub>2</sub>O volume fractions

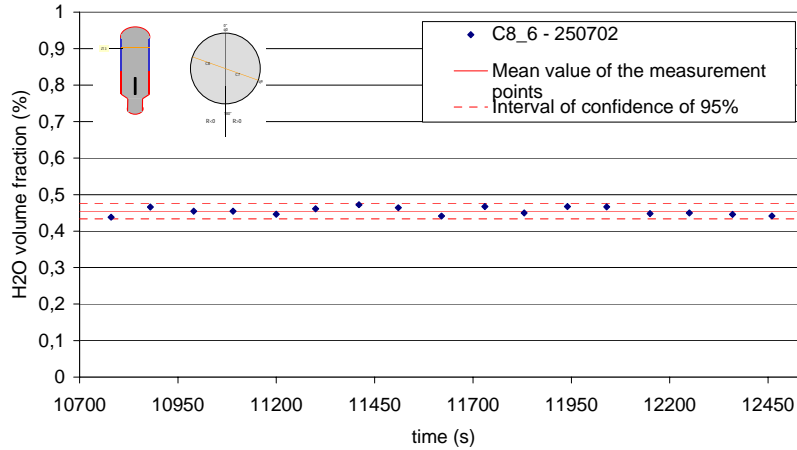


Figure15: Stability of the H2O volume fraction measurement during a steady-state near the TOSQAN symmetry axis.

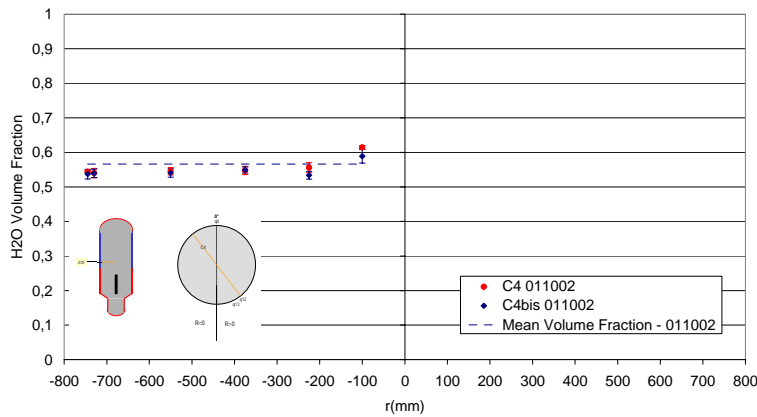


Figure 16: Repeatability of H2O volume fraction profiles : measurements performed during the steady-state of a TOSQAN test (steam injection region)

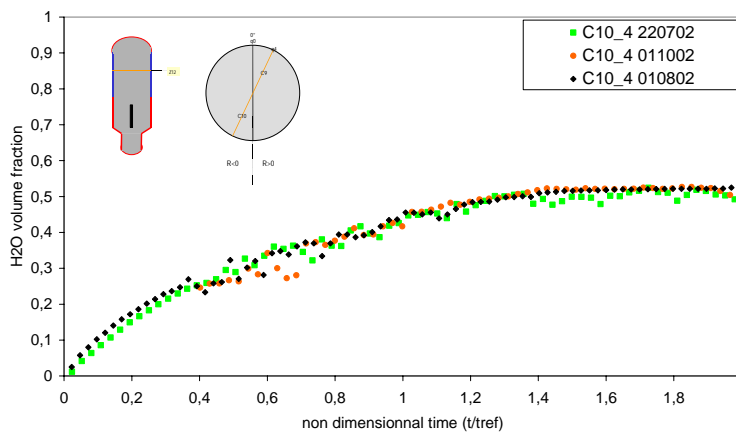


Figure 17: Repeatability of the time evolution of the H2O volume fraction during steam injection. Measurements performed on different days for the same TOSQAN test.  $t_{ref}=t(P=0.8bar)$