

# A Portable Calibration Gas Generator for H<sub>2</sub>O, HCl, NH<sub>3</sub> and Mercury

Peter Wilbring<sup>1</sup>, Martin Schmaeh<sup>2</sup>

<sup>1</sup> TÜV Immissionsschutz und Energiesysteme GmbH, Am Grauen Stein, D-51105 Köln

<sup>2</sup> IAS, Rödelheimer Landstraße 13A, D-60487 Frankfurt am Main

## Abstract

The calibration of emission measurement systems for water vapor, hydrogen chloride, ammonia and mercury is difficult and span gas is not available for every component. On the principle of the dynamic evaporation of liquids and the continuous addition of carrier gas, a portable calibration gas generator was developed. Linearity, accuracy and the reproducibility is comparable with the quality of certified cylinder span gas or even better. Besides a number of advantages over existing calibration methods, the system provides a calibration gas with similar constitution as flue gas especially for water content. Mercury chloride has been investigated up to a concentration of 150 µg/m<sup>3</sup>. Besides carrier gas flow variation, also time constant and the speciation of mercury under the influence of evaporator temperature has been examined.

## Introduction

The calibration of emission measuring systems for H<sub>2</sub>O, HCl, NH<sub>3</sub> and mercury shows a few difficulties: H<sub>2</sub>O is not available as test gas up to the required concentrations and the handling of HCl needs appropriate experience [1]. The wall adsorption effects of HCl, NH<sub>3</sub> and also HF even on heated surfaces of gas feeding components result in time lag, a dragging running behaviour and deviations of the reading, especially at low concentrations. Mercury as Hg<sup>0</sup> is available as test gas. But it is known, that the behaviour of HgCl<sub>2</sub> is completely different in terms of adsorption [2]. Moreover Hg<sup>0</sup> test gas is only suitable to check the photometer of the Hg-emission measuring system, but not the sample conditioning system. This demand has led to the development of the calibration gas generator HOVACAL.

## Principle of operation

The device works on the principle of the dynamic evaporation of liquids and the constant addition of carrier gas. A continuous flow of liquid is injected in an evaporator and mixed with a continuous carrier gas flow. Both liquid and gas flow are monitored as mass flows and therefore independent of temperature and pressure. The resulting concentrations can be calculated with the mixing equations given below.

The basic equation for water vapour concentration is:

$$c_{H_2O} = \frac{100}{1 + \left( \frac{v_{gas}}{f \cdot v_{liquid}} \right)} \quad (1)$$

where  $c_{H_2O}$  is the water vapour concentration in % V/V,  $v_{liquid}$  the liquid flow in g/min,  $v_{gas}$  the carrier gas flow in ml/min based on standard conditions and  $f$  the volume factor from liquid to gas; the numerical value for water is 1244,53.

The use of aqueous solutions of hydrogen chloride, ammonia or mercury chloride in place of purified water result in gas vapour mixtures. The concentration of the gas components in the aqueous solution is an additional parameter to the mix ratios of liquid and gas flows. This liquid concentration is usually given in mol/liter.

The basic equation for aqueous solutions of components like HCl, NH<sub>3</sub> and HgCl<sub>2</sub> up to concentrations of approximate 1 mol/l, based on wet gas is:

$$c_K = \frac{M_K \cdot n_K}{f + \left( \frac{v_{gas}}{v_{liquid}} \right)} \cdot 10^6 \quad (2)$$

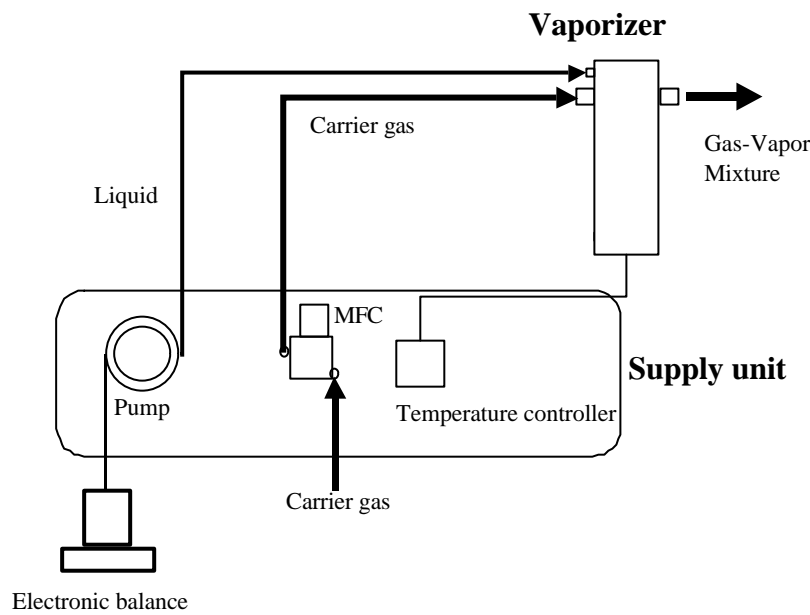
where  $c_K$  is the concentration of gaseous component in mg/m<sup>3</sup>,  $M_K$  the molecular mass of this component,  $n_K$  is the liquid concentration in mol/liter and  $f$  is the volume factor for water.

Is the concentration based on dry gas, the volume factor in equation (2) have to be omitted:

$$c_K = \frac{M_K \cdot n_K}{\left( \frac{v_{gas}}{v_{liquid}} \right)} \cdot 10^6 \quad (3)$$

### Principle of the device

The calibration gas generator consists of a portable supply unit, an evaporator and an electronic balance. Supply unit and evaporator are connected via electrical power cables, temperature signal, carrier gas and liquid supply lines. The construction is shown in diagrammatic form in Fig. 1.



**Fig. 1: Schematic representation of the calibration gas generator**

A peristaltic pump is used to pump the liquid into the evaporator from a liquid reservoir. The liquid is passed through a fine filter to keep the evaporator and gas vapour mixture free of contamination.

The mass of liquid pumped is dosed using a precision balance. The liquid flow is determined primarily by the speed of rotation and tube diameter of the pump.

The carrier gas is fed to the supply unit at an overpressure and a mass flow controller injects a continuous and constant flow into the evaporator.

The evaporator can be set up some meters away from the supply unit. It has a carrier gas connection and a liquid supply port. The temperature of the evaporator can be controlled on the temperature controller integrated into the supply unit.

The gas vapour mixture must be extracted while still hot to prevent condensation and associated losses of gas components or water vapour. This is done by either connecting a heated pipe to the evaporator or accommodating the entire evaporator in a larger heated unit, e.g. a measuring gas supply unit.

Due to the liquid metering with an electronic balance and the gas metering with a mass flow controller, both fluid flows are mass flows and the resulting concentration is independent of temperature and pressure.

The evaporator can be operated up to temperatures of 240 °C. Typical a temperature of 180 °C is used. At this temperature most of the sampling lines are operated. The temperature of the vaporisation is not critical, but the

only criterion is that the temperature is well above the temperature of dew point. With 180 °C this condition is fulfilled for water in any case and also for components like HCl, HF and NH<sub>3</sub> in conjunction with water vapour.

The working range for generating water vapour is defined in terms of three parameters and limited by the maximum power of the evaporator (800 W) . The presented device has characteristic, shown in Table 1.

**Table 1: Characteristic of HOVACAL evaporator**

Parameter	Minimum	Maximum	Optimum
Liquid flow rate in g/min	0,05	6	0,1 – 4
Carrier gas flow in l/min	3	10	4 - 7
Vaporisation temperature in °C	150	240	180 - 200
Water vapour concentration % V/V	0,6	70	1,7 - 55

Thus water vapour concentrations between 0 and 40 % V/V are generated in the optimum working range. For demand of higher water vapour content or higher carrier gas flow, the power of the evaporator can be enhanced.

## Results and analysis

A laboratory test and a field trial have been made to examine the accuracy and linearity for the components H<sub>2</sub>O, HCl, NH<sub>3</sub> and HgCl<sub>2</sub> [3, 4]. For verification of the concentration in laboratory, conventional methods have been used. In the field trial, calibrated continuous emission measuring systems have been used.

### Accuracy

In Table 2, the accuracy of the calibration gas generator for the different components is shown. The carrier gas flow was set at 300 l/h, the temperature of the evaporator at 180 °C. The nominal value, calculated with above mixing equations, was set at the calibration gas generator, the analytical result was achieved by the specific conventional method.

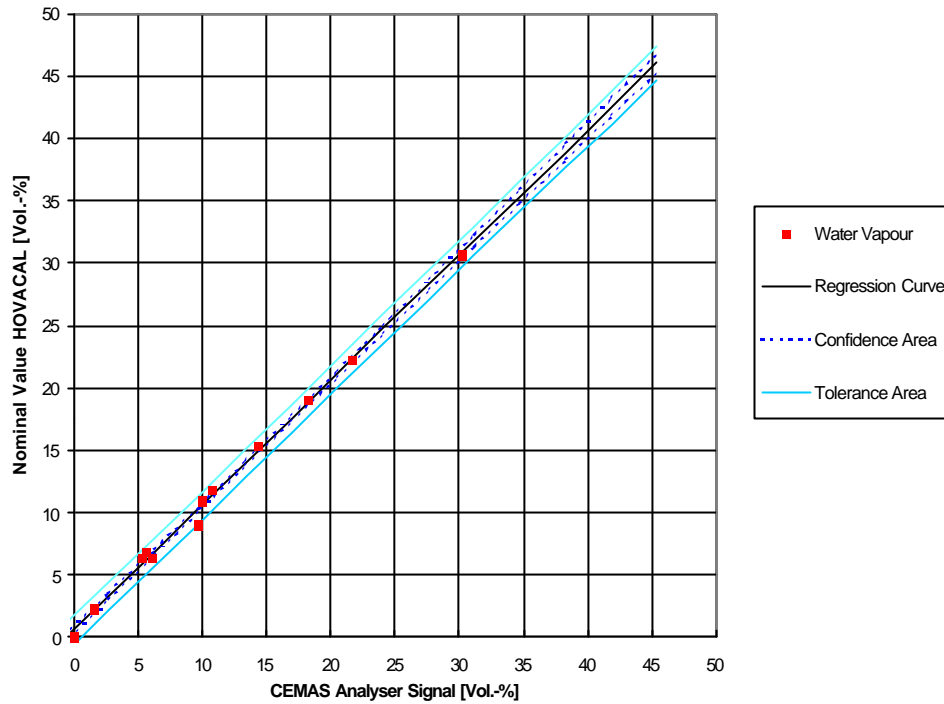
**Table 2: Accuracy of HOVACAL in terms of mean deviation**

Component	Measuring Range	Number of measurements	Standard deviation %	Slope
Water vapour	0 – 40 % V/V	27	1,62	1,002
Hydrogen chloride	0 –500 mg/m <sup>3</sup>	27	0,88	0,998
Ammonia	0 – 500 mg/m <sup>3</sup>	27	0,97	0,999
Mercury chloride	0 – 150 µg/m <sup>3</sup>	11	1,79	0,941

The standard deviation as a result of a linear regression, shows high statistical security and a slope of nearly one for each component. The error of the conventional method has not been compensated.

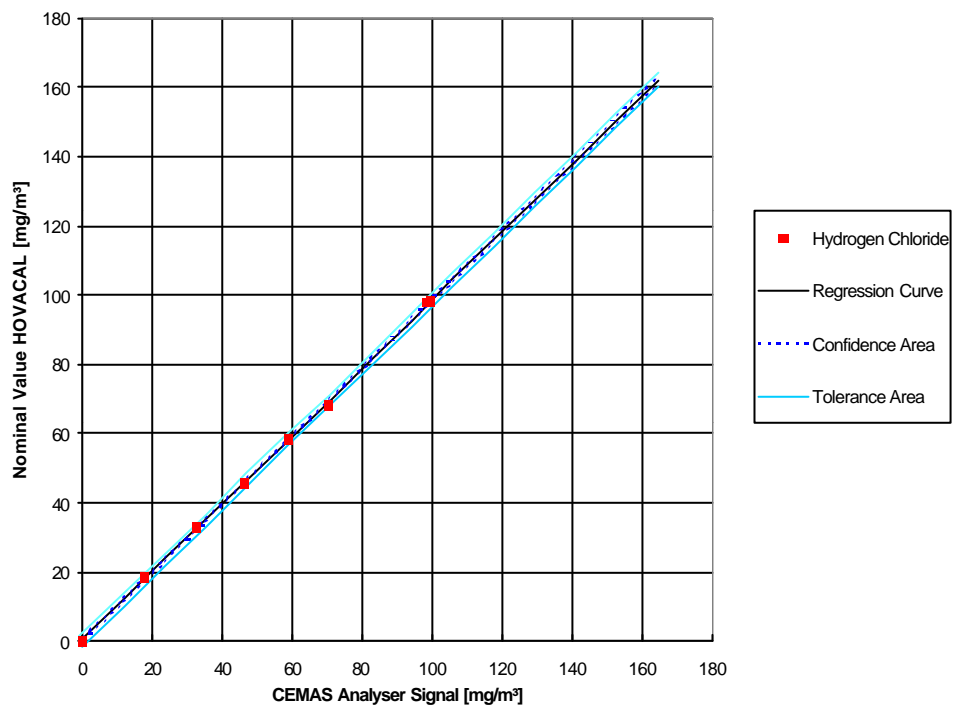
### Linearity

In Fig.2, 3 and 4 the linearity check for the different components are shown. A calibrated, continuous FTIR-analyser (CEMAS FTIR, ABB Automation Products) was used to monitor the test gas, generated by HOVACAL. The sampling system and measuring cell of the analyser was heated to 180 °C also temperature of evaporator and test gas. The evaporator was placed in the heated measuring gas supply unit of the analyser. The carrier gas flow was set at 360 l/min. As carrier gas purified air or nitrogen was used.



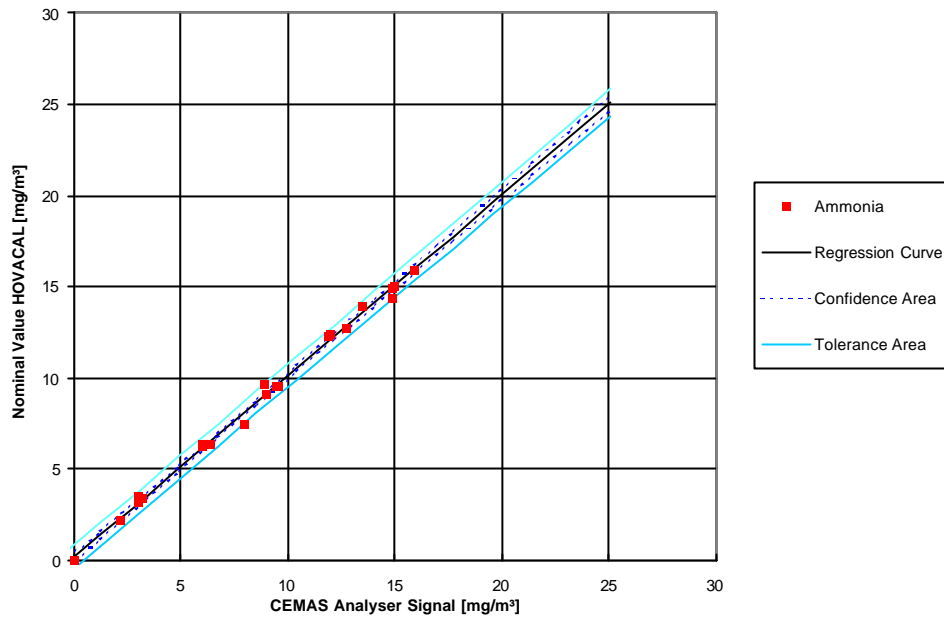
**Fig. 2: Linearity check of water vapour**

At 8 measuring points, 33 measurements were made. By linear regression a slope of 1,002 and a standard deviation of 0,544 % V/V was found.



**Fig. 3: Linearity check of hydrogen chloride**

At 6 measuring points, 24 measurements were made. By linear regression a slope of 0,982 and a standard deviation of 4,436 mg/m<sup>3</sup> was found.

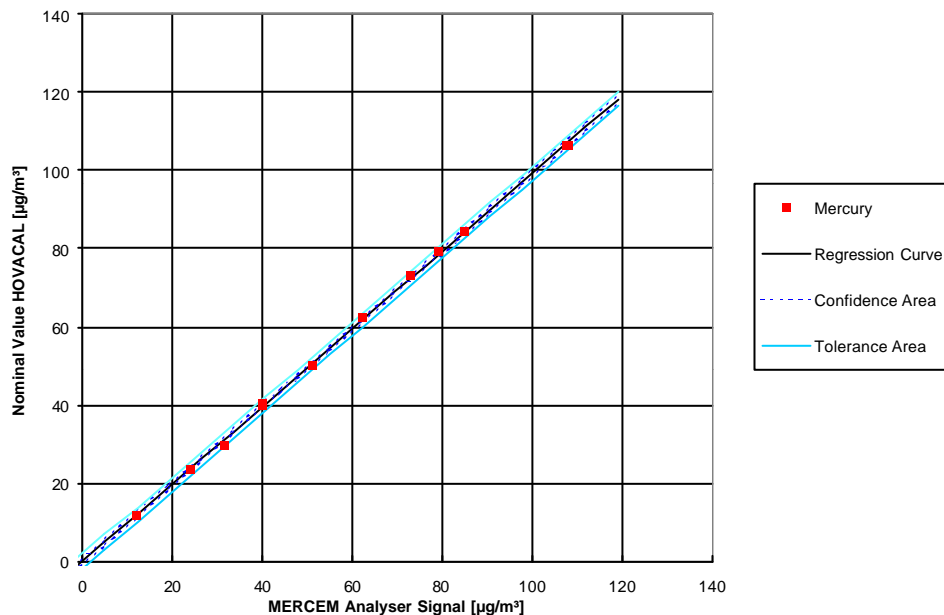


**Fig. 4: Linearity check of ammonia**

At 6 measuring points, 23 measurements were made. By linear regression a slope of 0,997 and a standard deviation of 4,4.833 mg/m<sup>3</sup> was found.

Due to the low vapour pressure of water and aqueous hydrogen chloride solution, the handling of this solutions is very simple. Aqueous ammonia solutions, especially at higher concentrations, cannot handled in an open bottle. A flexible bag system was designed for storage and handling them.

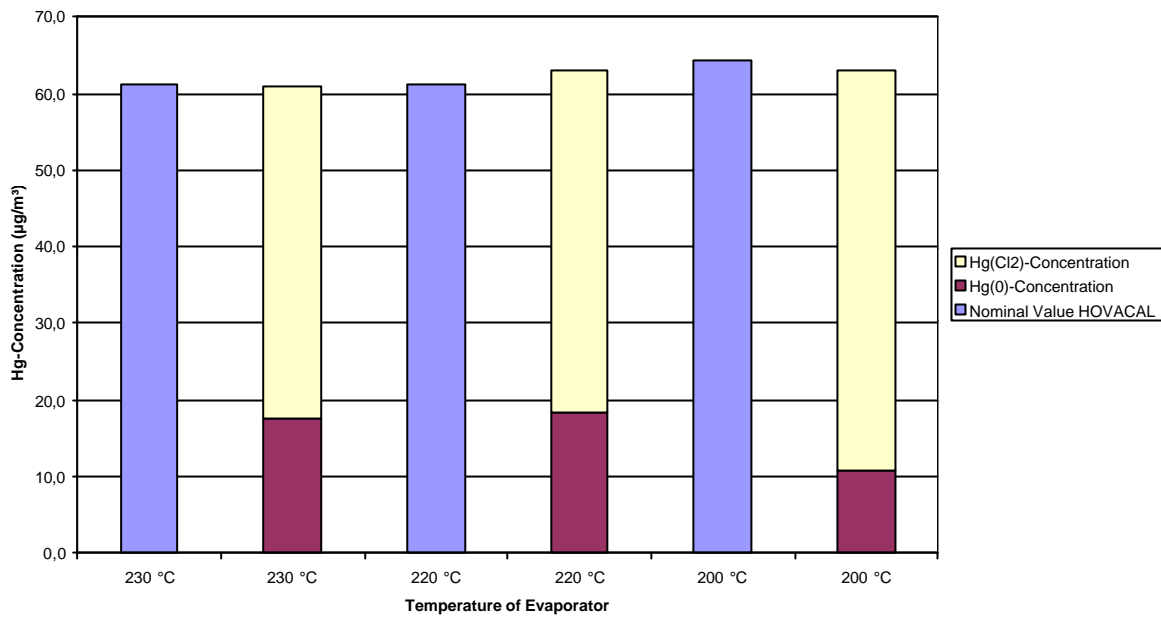
In Fig. 5, the linearity check for mercury is shown over a range of 100 µg/m<sup>3</sup>. The HOVACAL evaporator outlet was connected to a MERCCEM analyser (Sick UPA). The gas tube between the evaporator and the analyser inlet was thoroughly heated up to 180 °C to prevent cold bridges and wall adsorption.



**Fig. 5: Linearity check of mercury**

At 11 measuring points, 11 measurements were made. By linear regression a slope of 0,995 and a standard deviation of 0,709 µg/m<sup>3</sup> was found.

Fig. 6 shows the speciation analysis. The ratio between elementary Hg and HgCl<sub>2</sub> is between 20 and 30 %, depending on the temperature of the evaporator [5].



**Fig. 6: Speciation analysis of HOVACAL mercury test gas**

At lower temperatures, the ratio Hg<sup>0</sup>/HgCl<sub>2</sub> decreases. A hint, that thermal decomposition of HgCl<sub>2</sub> may occur at higher temperatures. The lower limit of temperature investigations is 180 °C, due to strong wall adsorption effects of mercury chloride.

## Conclusions

The HCl- and NH<sub>3</sub>-test gas, produced with the calibration gas generator HOVACAL is comparable with cylinder test gas. The humidity of the HOVACAL test gas can be adapted to the water content of the measuring gas. Therefore, calibration and measuring conditions can be made very similar, especially in the case, when instead of nitrogen or air, a span gas mixture of typical flue gas components is used. An additional advantage of the hot and wet span gas, is the reduced adsorption wall effect.

The range of water vapour covers the typical applications in continuous emission monitoring for calibration and cross sensitivities check.

The humidity of the generated mercury span gas can also adapted to the humidity of flue gas and allows besides the calibration of Hg-analysers also the check of the sampling system. Further investigations will be made in defined change of the ratio between Hg<sup>0</sup> and HgCl<sub>2</sub>.

## References

- [1] W. Jockel, C. Gökcek, H. Bollmacher: Stabilitätsuntersuchungen an HCl- und HF-Prüfgasen in Druckgasflaschen . Staub 47 (1987) 280 – 282
- [2] H. Braun, A. Gerig: Einfluß von Materialien bei der Beprobung quecksilberchlorid-haltiger Abgase. Staub 54 (1994) 167 – 170
- [3] P. Wilbring, Bericht über die Prüfung des Kalibriergasgenerators HOVACAL des Ing.-Büro Dr. Schmäh, Frankfurt, (1997), TÜV-Bericht 936/970001A
- [4] P. Wilbring, C. Röllig, Bericht über die Prüfung des Kalibriergasgenerators HOVACAL des Ing.-Büro Dr. Schmäh Frankfurt, für die Komponente Quecksilber, (1998) TÜV-Bericht 936/980001A
- [5] P. Wilbring, C. Röllig, Bericht über die Prüfung des Kalibriergasgenerators HOVACAL des Ing.-Büro Dr. Schmäh Frankfurt, für die Komponente Quecksilber, (2000) TÜV-Bericht 936/000001A

## Biographical detail of the authors

Dr. Martin Schmäh, Physicist, IAS Ingenieurbüro für Analysen- und Sensortechnik, Manufacturer of the calibration gas generator HOVACAL located in Frankfurt am Main, Germany . He works since 1987 in the area of gas analysis and since 1997 Manager of IAS.

Dr. Peter Wilbring, Chemist, TÜV Immissionsschutz und Energiesysteme GmbH, D-51101 Köln, Germany. He works since 1990 in the field of environmental protection especially in the area testing of continuous emission measurement and ambient air measurement systems.