

QUANTITATIVE GAS ANALYSIS IN VACUUM SYSTEMS

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For the determination of small gas quantities, gases are admitted to a vacuum system under dynamic pumping conditions and a great number of mass spectra are recorded together with the total-pressure gauge readings. A special calibration procedure has been developed, based on admittance of a calibrated gas-burst into the analytical chamber. The apparatus and the calibration method are described and an example for the analysis of a N_2 -CO-CO₂ mixture is given, showing that even complex gas-mixtures can be identified and analysed with errors of less than 2%.

Gas analysis, Calibration, Mass spectrometry

INTRODUCTION

Instruments for the measurement of low-density gases are mostly calibrated in terms of "pressure". In practice, however, it may be more desirable to know accurate values of the density, of the gas flux or even of the amount of gas. In this contribution we deal with gas-quantity measurements. Therefore, a suitable calibration method should be based rather on a calibrated gas quantity than on a pressure standard.

There are two possibilities for quantitative measurements of a small gas amount: the static and the dynamic method. Fig. 1 allows a simplified comparison. In the static method, a vacuum chamber with known volume V is evacuated to an ultimate pressure p_0 and then the pump is valved off. Now the gas to be measured is admitted and from the increase of pressure $\Delta p = p - p_0$ vs. time Δt , the gas flux, q , as well as the amount of gas, m , can be derived:

$$q = V \Delta p / \Delta t \quad (1)$$

and

$$m = V \Delta p. \quad (2)$$

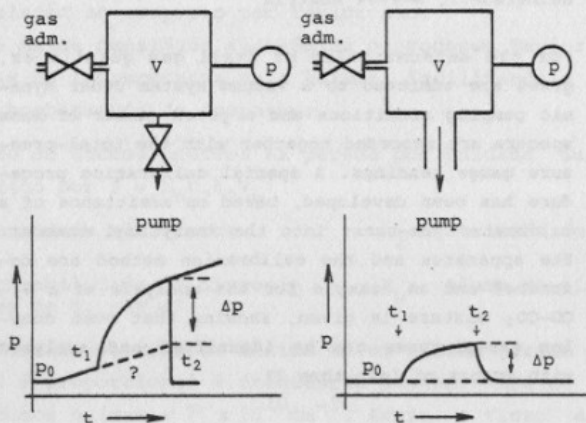


Figure 1: Static vs. dynamic method (V = volume, S = effective pumping speed, Δp = increase of pressure due to gas admittance).

In this method, data evaluation appears to be very simple, especially if the background is constant. In practice, however, one has to consider the various reactions of the gases with the hot filament of the gauge as well as ad- and desorption processes at the surfaces. Furthermore, the pressure difference Δp is relatively high (compared to the pressure p_0) and - consequently - a non-linear response of the gauge may give rise to a large error.

In the dynamic method, pumping is maintained continuously. Therefore, for a given flux or gas amount, the maximum pressure increase is smaller than in the static method, and it is more likely to achieve a constant background. Furthermore, as the sojourn times of the gas molecules in the chamber are much shorter, the probability for reactions of the admitted gases are reduced considerably. In this method, the flux can be calculated from the pressure increase, Δp , and the effective pumping speed, S_{eff} , as

$$q = \Delta p S_{eff} \quad (3)$$

and the amount of gas, m , can be determined by integration between two properly chosen time marks,

$$m = \int_{t_1}^{t_2} \Delta p S_{eff} dt. \quad (4)$$

Even in this method problems may arise, e.g. the background pressures $p(t_1)$ and $p(t_2)$ may differ due to changes in outgassing, or the "true" background pressure between t_1 and t_2 (inaccessible for a direct measurement) may differ from $p(t_1)$ or $p(t_2)$. However, the dynamic method offers a number of advantages, especially if oxygen-bearing gases have to be investigated. This method is used in our work.

APPARATUS

The apparatus used in our measurements is sketched in Fig. 2. The all-metal system consists mainly of a small chamber with a sample heater and a special tweezers-manipulator /1/, and contains the

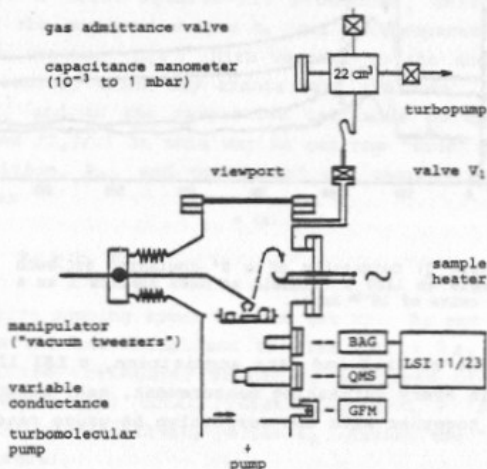


Figure 2: Apparatus used for the measurements of small gas-quantities.

necessary measuring instruments (a hot cathode ionization gauge of the Bayard-Alpert type and a quadrupole mass spectrometer). It is pumped by a 170 l/s turbomolecular pump, and backed by a catalysator-baffled rotary pump. Between analytical chamber and pump a variable conductance is installed, which can be set between 0,8 and 22 l/s (all values N_2 -equivalent).

A number of samples can be stored inside the chamber within the reach of the manipulator. A large viewport serves for identifying the samples and for controlling the manipulator movement. For outgassing, the samples are transferred onto the heater (in most cases a simple Mo-strip as used in evaporation plants); outgassing temperatures up to 1800 K can be chosen and outgassing may last from a few seconds to one hour. In order to keep the background pressure during the sample measurements as constant as possible, the Mo-strip is heated many hours in advance, allowing to achieve temperature equilibrium and low outgassing. As an example, the outgassing of a D^+ -implanted TiC-POCO sample at 1120 K is shown in Fig. 3.

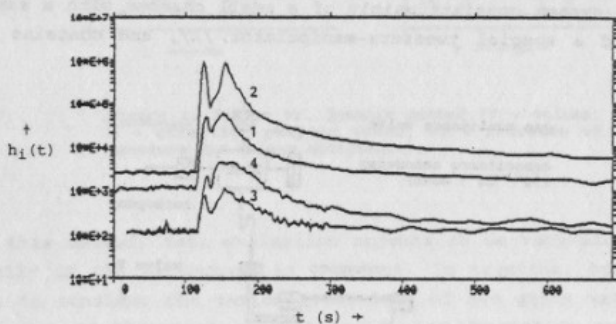


Figure 3: Outgassing of a D^+ -implanted TiC-POCO sample at 1120 K (signals at mass numbers 1 to 4 in units of 10^{-10} Amps).

For spectrometer control and data acquisition, a LSI 11/23 computer is used. In every outgassing measurement, many hundred spectra are collected together with the respective BA-gauge readings.

SPECTRUM DECOMPOSITION AND DATA EVALUATION

For data evaluation it has to be considered that every single mass spectrum h_i is caused by a superposition of the individual

spectra of the gases present in the ion source. In a simplified form, a single spectrum can be written as

$$h_i = \sum_k \epsilon_k P_k Q_{ik} \quad (5)$$

with h_i ... peak height at mass number i ,
 P_k ... partial pressure of gas with index k ,
 ϵ_k ... sensitivity for gas k (relative to N_2),
 Q_{ik} ... "cracking pattern" of gas k (= probability to find an ion with mass number i), normalized to give $\sum_i Q_{ik} = 1$ for any gas k .

After the outgassing, the measured values of the total pressure as well as the single mass spectra are integrated according to Eq. (4):

$$P = \int_{t_1}^{t_2} \Delta p(t) dt \quad (6)$$

and

$$I_i = \int_{t_1}^{t_2} h_i(t) dt. \quad (7)$$

In the next step, the decomposition of the integral spectra I_i is done via a least-squares-fit procedure, using individual weights for the measured values h_i and the (separately measured) "calibration factors" Q_{ik} . (With respect to the accuracy of the cracking patterns, which may change with pressure, time, pumping speed, etc., and to the respective influence on the achievable accuracy, see /2,3/.) In this way we get the "true" partial-pressure composition, P_k , and the "true" gas composition m_k can be calculated as

$$m_k = P_k S_k \quad (8)$$

(S_k = effective pumping speed for the gas k). P_k and m_k are relative figures and are normalized to give $\sum_k P_k = \sum_k m_k = 1$. In the final step, the (relative) values P_k are used to correct the (still N_2 -equivalent) total pressure integral P (see Eq. (6)) for the different sensitivity values ϵ_k , giving the "true" total-pressure integral,

$$P_t = P \sum_k (P_k / \epsilon_k) / \sum_k P_k, \quad (9)$$

and, in a similar way, the respective "true" amount of gas, m_t .

CALIBRATION PROCEDURE

As outlined above, in our method the mass spectrometer is used for the determination of the relative gas-composition only, and the absolute values are derived from the BA-gauge readings. There are many reasons for this procedure, introduced more than a decade ago /4/. One reason is that, compared to a mass spectrometer, the long-time drift in the ion production rate (depending e.g. on filament position) and also in the ion-collection efficiency of a BA-gauge are much smaller. In particular, surface- and space-charge effects, and a possible drift in lens potential and in SEM gain in the mass-spectrometer may change the absolute heights of the peaks and thus alter the calibration.

On the other hand, our method requires an absolute calibration of the term pressure times pumping speed, according to Eq. (4), making in-situ calibration of the BA-gauge together with the conductance necessary. For this purpose, and also for checking the properties of the mass-spectrometer, a special "gas burst" calibration technique has been developed. The calibration unit, shown in the upper section of Figure 2, consists mainly of a calibrated volume (22 cm^3) including a membrane manometer of the capacitance type, allowing accurate measurements of the total pressure between 10^{-3} and 1 mbar. The gas quantity in this chamber is simply calculated from the product of volume and pressure, and - by successively admitting different gases into the chamber - even calibrated gas-mixtures can be produced and maintained until they are needed.

These calibrated gas quantities can be admitted to the analytical chamber at any time by opening the (electrically driven) valve V_1 . The "length" of the burst can be chosen by a proper setting of the conductance of this valve. The all-metal system is evacuated by a 50 l/s turbomolecular pump.

The capability of our method is illustrated by the analysis of a calibrated mixture of N_2 , CO and CO_2 (one of the worst cases for a mass-spectrometric gas analysis). Within a relative error of $\pm 10\%$ equal amounts of every gas were taken (i.e. $33 \pm 3\%$ in the mixture). This gas mixture was admitted to the analytical chamber and was treated as an "unknown gas", i.e., the total pressures and the peak heights measured with the mass spectrometer were recorded and computed as in the case of an unknown sample. Fig. 4 shows

the signals at the 4 most significant mass numbers. Data evaluation was based on cracking patterns, measured separately for the

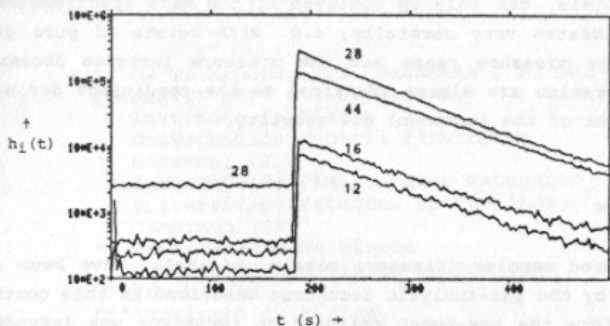


Figure 4: Admittance of a N_2 -CO-CO₂ mixture for calibration purposes (signals at mass numbers 12, 16, 28 and 44 in units of 10^{-10} Amps).

pure gases. Table I shows the integral spectrum for the admitted gas mixture, $I_1 = FM(Z)$, at the 7 mass numbers chosen between 12 and 44, the values $m_k = \text{AMOUNT OF GAS (PER CENT)}$ together with the calculated external errors and the quantity $m (= \text{TRUE AMOUNT OF GAS})$ and its composition (all values in STD CCM = mbar).

Table I: Results obtained from the analysis of the N_2 -CO-CO₂ mixture.

M	Z	FM(Z)	DFM(Z)	FN(Z)	FC(Z)	DIF(Z)	DEL0
12	1	62.059	1.030	62.0591	62.6002	-0.5411	0.2761
14	2	76.707	1.077	76.7067	78.0409	-1.3341	1.5339
16	3	103.542	1.094	103.5424	109.2520	-5.7096	27.2629
22	4	20.494	1.021	20.4936	23.3570	-2.8634	7.8654
28	5	1952.975	2.642	1952.9746	1952.4752	0.4994	0.0357
29	6	18.453	1.024	18.4533	17.1639	1.2893	1.5840
44	7	1145.626	1.966	1145.6259	1143.7786	1.8473	0.8830

CHI SQUARED = 39.44 DEGREES OF FREEDOM = 4 RATIO EXT./INT.ERROR = 3.1401

I	B(I)	ERROR
1	11.0025	0.530E+00
2	8.5347	0.325E+00
3	14.3295	0.763E-01

AMOUNT OF GAS (PER CENT)

	N2	CO	CO2
	35.53	27.56	36.91
ERROR	1.71	1.70	0.20

AMOUNT OF GAS (N2-E0) = 0.187E-03 STD-CCM
TRUE AMOUNT OF GAS = 0.171E-03 STD-CCM

GAS AMOUNT (STD-CCM) :

N2	: 0.609E-04
CO	: 0.472E-04
CO2	: 0.632E-04

From a series of test measurements we know that standard deviations of less than 2 % in the gas composition, as obtained in this analysis, can only be achieved if the mass spectrometer has been calibrated very carefully, e.g. with bursts of pure gases, and if the pressure range and the pressure increase chosen for the calibration are almost identical to the conditions during the measurement of the (unknown) gas quantity.

CONCLUSION

Many hundred samples (glasses, metals, minerals) have been investigated by the gas-analytic technique described in this contribution. Before the gas-burst calibration technique was introduced, the absolute accuracy was related to the BA-gauge accuracy only, and was not much better than within a factor of 2. In these measurements we have learned that cracking patterns may change between calibration and measurements, especially if the duration of the calibration and/or if the pressure range chosen differ too much from the respective values of the analytical measurement (i.e., the gas quantity of the calibration burst and its length should be very similar to the respective value of the analysis). Only with very careful calibration, as with the gas-burst technique, we could improve the accuracy of our fit-procedure to better than ± 2 %, even for mixtures of oxygen-bearing gases. The absolute accuracy of our present method, mainly given by the accuracy of the capacitance manometer, is assumed to be better than ± 5 %.

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