

Hydrogen Analysis by Vacuum Hot Extraction (VHE)

Key words

Vacuum hot extraction, mass spectrometry, hydrogen content, diffusion

Fields of application

Determination of H₂ content in solid materials (e.g. solved in quartz glass, 0.5 µg/g – 1000 µg/g OH; trapped H₂ (> 300 °C) in steel and nonferrous metals, 0.1 µg/g – 1000 µg/g). H₂ degassing between 20 °C and 1550 °C, Effective diffusion coefficients of H₂ in specimens of quartz glass or metals are determined by isothermal VHE using a numerical fitting procedure.

Methodology and instrumentation

Thermally induced high vacuum gas extraction and simultaneous detection of H₂ and other volatile species by means of quadruple mass spectrometry

Items tested

Bulk samples < 5 x 5 x 40 mm³ (e.g. metals) or powders (≈ 1 mg – 500 mg, dependent on H₂ content)

Quantities / characteristics tested

Detection limit of degassing rate ≈ 1 nmol/min

Heating rates of furnaces:

- (1) Rh wire, ceramic tube ≤ 40 K/min up to T_{max} = 1550 °C
- (2) Halogen spotlight, quartz glass tube ≤ 300 K/min up to T_{max} = 900 °C

H₂-sensitivity: 0.14 A min / mol

Ascertainable range of diffusion coefficients: 10⁻¹³ cm² s⁻¹ – 10⁻⁵ cm² s⁻¹
(for H₂ in quartz glass: 10⁻⁷ cm² s⁻¹ – 10⁻⁵ cm² s⁻¹ in the temperature range T = 300 °C – 1500 °C)

Uncertainty / reliability of results

ΔC ≈ 15 %, ΔD ≈ factor 5

Qualification and quality assurance

Developed and assembled by BAM, no comparable facility known, at least in Germany.

Unique measurement capabilities, a.o. for hydrogen in the presence of structurally associated water.

Significantly improved detection capabilities (factor 10 and better).

Validation of VHE measurements by comparison with IR-, RAMAN- and NRA-experiments.

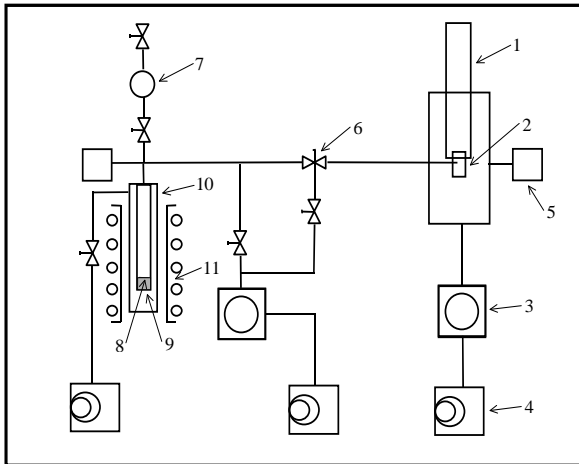
Determination of effective diffusion coefficients of isothermal VHE degassing kinetics for the first time world wide. Long-time experience in research and close co-operations with university institutes and major glass producers.

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Further information

Vacuum Hot Extraction (VHE)

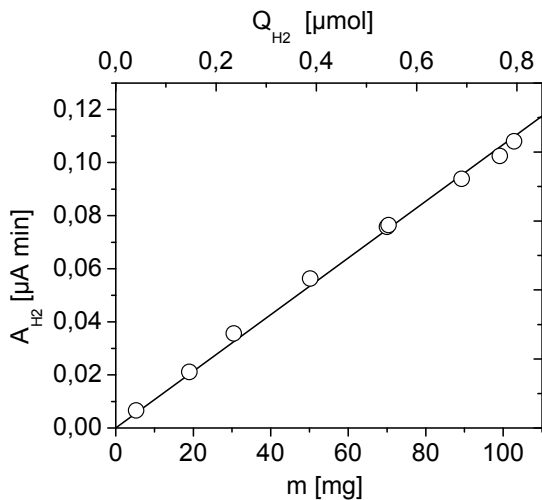
Vacuum hot extraction coupled with mass spectrometry allows the simultaneous detection of physically and chemically solved H₂, which escapes from specimens under investigation during heating in vacuum.



- Scheme of VHE
- 1 – quadruple mass spectrometer,
 - 2 – ion source,
 - 3 – high vacuum turbo molecular pump,
 - 4 – rotation pump,
 - 5 – pressure gauge,
 - 6 – heated gas inlet,
 - 7 – calibration system,
 - 8 – sample,
 - 9 – quartz glass crucible,
 - 10 – Al₂O₃-tube,
 - 11 – Rh furnace

Hydrogen degassing and content

Despite the most common use of VHE to reveal temperature ranges of enhanced volatile degassing activity, calibration of VHE allows to measure the degassing rate quantitatively. Integrating of this rate yields the total amount of released gas and its initial content. Preferably quartz glass of known H₂ content or high purity TiH₂ are used as reference materials for calibration [1].



- Linearity test for VHE H₂ detection using a reference quartz glass sample containing 133 µg/g OH (chemically dissolved H₂, detected by IR spectroscopy).
- Open circles: total amount of released H₂ in terms of the time-integrated VHE MS-ion current, A(H₂), as a function of sample mass, m.
- Upper abscissa: H₂ content Q(H₂), related to the sample mass, m.
- Line: best linear regression fit through the point of origin.

Hydrogen diffusion

In addition, determination of H₂ effective diffusion coefficient is possible [2]. For this examination, the use of fused silica powder of 40 µm and 2000 µm in size is most appropriate. The samples are heated up to a certain temperature. Then, this temperature is kept constant and the decay of the degassing rate is measured. By using numerical fitting procedures (simulated annealing method) the diffusion coefficient is calculated automatically. Another advantage consists in a possible minimisation of defaults which can occur by reaching the isotherm condition. This is realized by calculating a virtual starting time of the isothermal degassing process. This method can be applied to compact metal specimens using adapted mathematical models and calculation procedures.

Literature

- [1] P. Ried, M. Gaber, K. Beyer, R. Müller, H. Kipphardt, T. Kannengießer: Thermo Analytical Investigation of Hydrogen Effusion Behaviour – Sensor Evaluation and Calibration, *Steel Research International* **82** (2011) (1), p. 14
- [2] P. Gottschling, M. Gaber, R. Müller: Water concentration and diffusivity in silicate crystals, glasses, and melts obtained by vacuum extraction powder method, *Glass Sci. Technol.* **78** (2005) (2), p. 76