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**On the corrosion of copper in
pure water**

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

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ON THE CORROSION OF COPPER IN PURE WATER.

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ABSTRACT.

Due to a remarkable publication by Hultquist questioning well known thermodynamic data the corrosion of copper in distilled water has been studied. No hydrogen evolution was observed during an exposure period of 61 days using a gaschromatographic technique. Cu_2O was the only corrosion product detected by means of ESCA and cathodic reduction. The corrosion rates obtained for two different qualities are much lower than corrosion rate measured in the study by Hultquist and is ascribed to the reaction between the copper foils and rest oxygen initially present in the water. In conclusion the present investigation confirmed well established thermodynamics, which means that oxidation of copper by pure deoxygenated water under the formation of hydrogen as proposed by Hultqvist is not thermodynamically feasible.

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SUMMARY.

Hydrogen evolution by corrosion of thin copper foils in deaerated distilled water was studied in laboratory experiments using a gaschromatographic technique.

The corroded copper surface was analyzed by ESCA and cathodic reduction.

No hydrogen evolution was observed during an exposure time of 61 days. The formation of the corrosion product Cu_2O is ascribed to a reaction between the copper surfaces and small amounts of residual oxygen in the reaction vessels.

INTRODUCTION

Copper has been proposed as a reasonably inert material for the production of canisters for radioactive waste. The main advantage of copper is its stability in ground water (Cu is a noble metal). A thorough discussion of the stability of copper and possible corrosion reactions has been given in technical reports published by the Swedish Nuclear Fuel and Waste Management Co (The Swedish Corrosion Institute and its reference group 1978, 1983). The work has also been summarized by Mattsson (1984). However, the corrosion of copper in pure oxygen free water has been disputed in a recent publication (Hultquist 1986). In his study the corrosion of copper in initially aerated distilled water was followed by monitoring the hydrogen (H_2) concentration in the reaction vessel with a solid electrolyte probe described by Lyon and Fray (1984), working on the basis of a concentration cell. From the voltage versus time of exposure plot the H_2 production by a 99.7 wt% copper foil with surface area 1460 cm^2 was found to be $2.2 \cdot 10^{-6} \text{ g} \cdot \text{h}^{-1}$, corresponding to a corrosion rate of $0.1 \mu\text{g} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$. In fact the highest partial pressure of H_2 is close to 0.1 atm. This observation is at variance with the very well established thermodynamic data for the Cu- H_2O - O_2 system as shown e.g. in potential-pH diagrams.

Hultquist indicates that his finding is a result of a non-reversible cathodic reaction for which "we cannot predict an upper hydrogen pressure (in an oxygen-free corroding system)". This statement is of course a violation of the second law of thermodynamics, a fact which seems to have escaped the author, the reviewers and the editor of Corrosion Science. The paper might have been left to obscurity were it not for the nuclear waste aspects. In fact the results of Hultquist were first reported in an interview in a Swedish weekly technical journal "Dagens Industri" (Hultquist 1984). References to Hultquist's article have also been made by various organizations (including some universities) when reviewing the Swedish nuclear waste management research program.

Ignorance of thermodynamics seems to be more wide-spread than we thought possible. Due to the important application of copper canisters for final storage of nuclear waste we have made a reinvestigation of the copper corrosion by pure deoxygenated water using an alternative technique to monitor hydrogen. In this way we will also demonstrate what has gone astray with Hultquist's experimental work.

EXPERIMENTAL.

The copper foil qualities used in this investigation are Merck >99.7 wt% (0.1 mm thick, 1600 cm^2 surface area) and Alfa 99.9995 wt% (0.025 mm thick, 600 cm^2 surface area).

The water used was deionized, double distilled in a quartz apparatus and deaerated by purging with Ar (AGA SR-quality) containing less than 1 ppm oxygen. This procedure does not seem to have removed all oxygen as seen from our discussion below. The foils were rinsed with methanol followed by ethanol and

quickly dried in a stream of Ar before use. The foils were placed in glass vessels (1365 cm³ volume) in such a way that all parts of the surface areas were accessible for contact with water and the vessels flushed with Ar (AGA SR-quality). Water was thereafter transferred to the copper containing vessels by applying an overpressure of Ar to the water reservoir. The water and gas volumes of each vessel were 900 and 465 cm³ respectively. Assuming the solubility of O₂ and H₂ to be 1.4 and 0.85 mmol·dm⁻³ respectively at 25°C (CRC 1965) more than 98% of these gases should be in the gas phase of the reaction vessels. To monitor the H₂ the vessels were connected to the sampling loop of an Argograf (AGA) allowing small volumes of the gas phase to be transferred to the carrier-gas stream (Fig. 1). The gaschromatograph was calibrated by applying the same sampling procedure to a corresponding vessel containing Ar and known concentrations of H₂.

At the end of the experiment the exposed copper foils were quickly dried in a stream of Ar and small areas of the surfaces analyzed by ESCA and cathodic reduction. Larger samples (50 cm² surface area) were immersed for 120 minutes in 50 cm³ of a thoroughly deaerated 1 mol·dm⁻³ HClO₄ solution. The solutions were thereafter analyzed for copper by atomic absorption spectrophotometry. Unexposed copper foils were used to obtain reference solutions.

RESULTS.

The exposure lasted for 61 days and no H₂ was detected during the time of the experiment. The detection limit was approximately 10 ppm (Figs.2,3). To ensure that the absence of H₂ was not due to any leakage small volumes of H₂, yielding a concentration in the range 100-300 ppmv in the gas phase of the reaction vessels were added and the H₂ concentration monitored for 12 days. No change in concentration i.e. no leakage was observed (Fig.4).

The two species present on the surface of the exposed copper foils were, according to the ESCA data Cu and Cu₂O. The result of the ESCA measurements was corroborated by the potential of the cathodic reduction, showing that Cu₂O was the only corrosion product. The thickness of the corrosion product layer on small areas of the most corroded parts of the copper foils was calculated from the integrated current during the time of reduction (Zakipour 1987). The results are given in table 1. The amount of Cu₂O going into solution in 1 mol·dm⁻³ HClO₄ from exposed samples are summarized in table 2.

Discussion.

The surface of the exposed copper foils were unevenly corroded, large areas were seemingly unaffected whereas smaller areas were clearly discoloured. The cathodic reduction was carried out on 0.5 cm² samples of the discoloured parts and the results obtained from dissolving the corrosion products in 1M HClO₄ probably better characterize the average thickness of the corrosion product layer. The ratio between the corrosion depths measured by the two methods is approximately 10. A maximum

pitting factor of 25 was assumed by the Swedish Corrosion Institute (1978) in the previous report on copper corrosion.

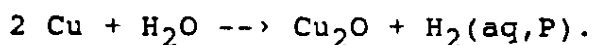
Based on the detection limit of 10 ppm H_2 and the reaction $H_2O + 2Cu \rightarrow Cu_2O + H_2$ the upper limits for the copper corrosion were calculated and are given in table 3 together with the average corrosion rates calculated from the dissolution data in table 2.

It is quite clear, based on the upper limit for hydrogen production, that the amount of copper corrosion caused by oxidation of water is at most $4 \cdot 10^{-5} \mu g \cdot cm^{-2} \cdot h^{-1}$. By using an alternative method Simpson and Schenk (1987) have decreased the detection limit of hydrogen to $3.7 \cdot 10^{-8} g \cdot h^{-1} \cdot m^2$ as compared to $0.1 \mu g \cdot cm^{-2} \cdot h^{-1}$ reported by Hultquist.

Corrosion may be caused by oxygen present in the reaction vessels i.e. according to the thermodynamically feasible reaction $2Cu + 1/2 O_2 \rightarrow Cu_2O$, the total amount of oxygen required by the mass balance of the corrosion products are given in table 4. As can be seen if the deoxygenation by Ar-purging was less efficient than approximately 97%, which is quite probable as no extreme measures were taken, the oxygen content of the reaction vessels would be sufficient to explain the corrosion. The higher rate of corrosion of the Alfa 99.9995% copper foil with the smaller surface area also gives support to the assumption of oxygen corrosion. The corrosion rates calculated from dissolution of the corrosion product Cu_2O from the exposed copper surfaces in our study are at least 5 times smaller than the corrosion rate given by Hultquist. It should be noted that more oxygen was initially available per unit surface area in the work of Hultquist and this probably accounts for the higher rate of corrosion observed in his experiments.

Our results clearly put doubts on Hultquist's method of measuring hydrogen. It is to be noted that the long time stability of the electrolyte probe has not been satisfactorily demonstrated as the longest time of exposure in the work of Lyon and Fray is 28 hours. A likely explanation of the time dependence observed by Hultquist is that his emf system gradually deteriorated.

By using standard free energies of formation of Cu_2O and H_2O we can calculate the highest possible partial pressure of H_2 for the reaction



We obtain $P(H_2) = 3 \cdot 10^{-18}$ atm

The concentration of molecular hydrogen in the near surface atmosphere has been determined to be approximately 0.65 ppmv and the concentration in water $0.44 \text{ nmol} \cdot \text{dm}^{-3}$ (Herr and Barger 1978) which makes oxidation of copper by water thermodynamically impossible.

CONCLUSIONS.

No hydrogen evolution by corrosion of copper in distilled water was observed during an exposure period of 61 days.

The corrosion product, determined by ESCA and cathodic reduction to be Cu_2O , is most probably formed in a reaction with small amounts of residual oxygen in the reaction vessels.

The following claims by Hultquist are erroneous

1. Hydrogen is evolved during corrosion of copper in water i.e. copper is oxidized by water
2. The escape rate of hydrogen from the corroding system is of decisive importance for the corrosion kinetics in water are erroneous.

The equilibrium pressure of H_2 according to the equation $2 \text{Cu} + \text{H}_2\text{O} \rightleftharpoons \text{Cu}_2\text{O} + \text{H}_2$ is $3 \cdot 10^{-18}$ atm, which is certainly much lower than the pressure of H_2 in any aqueous system. Hence corrosion by this reaction is not thermodynamically feasible.

ACKNOWLEDGEMENTS.

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Table 1

Thickness of corrosion product layer by cathodic reduction.

Sample		Thickness (Å)
Merck	(1)	1347
>99.7	(4)	484
Alfa	(2)	4613
99.9995%	(3)	3229

Table 2

Corrosion products dissolved in 1M HClO₄.
(50 cm² surface area, 50 cm³ solution)

Copper quality	Dissolved Cu mg·dm ⁻²	Average corrosion layer thickness (Å)	Comments
Merck > 99.7%	2		as received
	21.5	235	discoloured surface
	19.6		
	21.5		
	11.4	132	slightly discoloured surface
	15.0		
9.0			
Alfa 99.9995%	30	354	discoloured surface
	40		
	25		

Table 3

Average Cu corrosion rate calculated from dissolution of corrosion products and H₂ evolution at the detection limit 10 ppm.

Copper quality	Corrosion rate ($\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$)	
	corrosion prod	H ₂ (detection limit)
Merck > 99.7%	0.014	$1.1\cdot 10^{-5}$
	0.0082	
Alfa 99.9995%	0.021	$3.6\cdot 10^{-5}$

Table 4

Oxygen consumption from average corrosion rates.

Cu-quality	O ₂ consumed mg	Req initial O ₂ conc in gasphase %	Purging efficiency %
Merck > 99.7%	4.3	0.65	96.4
	2.4	0.36	98.0
Alfa 99.9995%	1.9	0.30	98.3

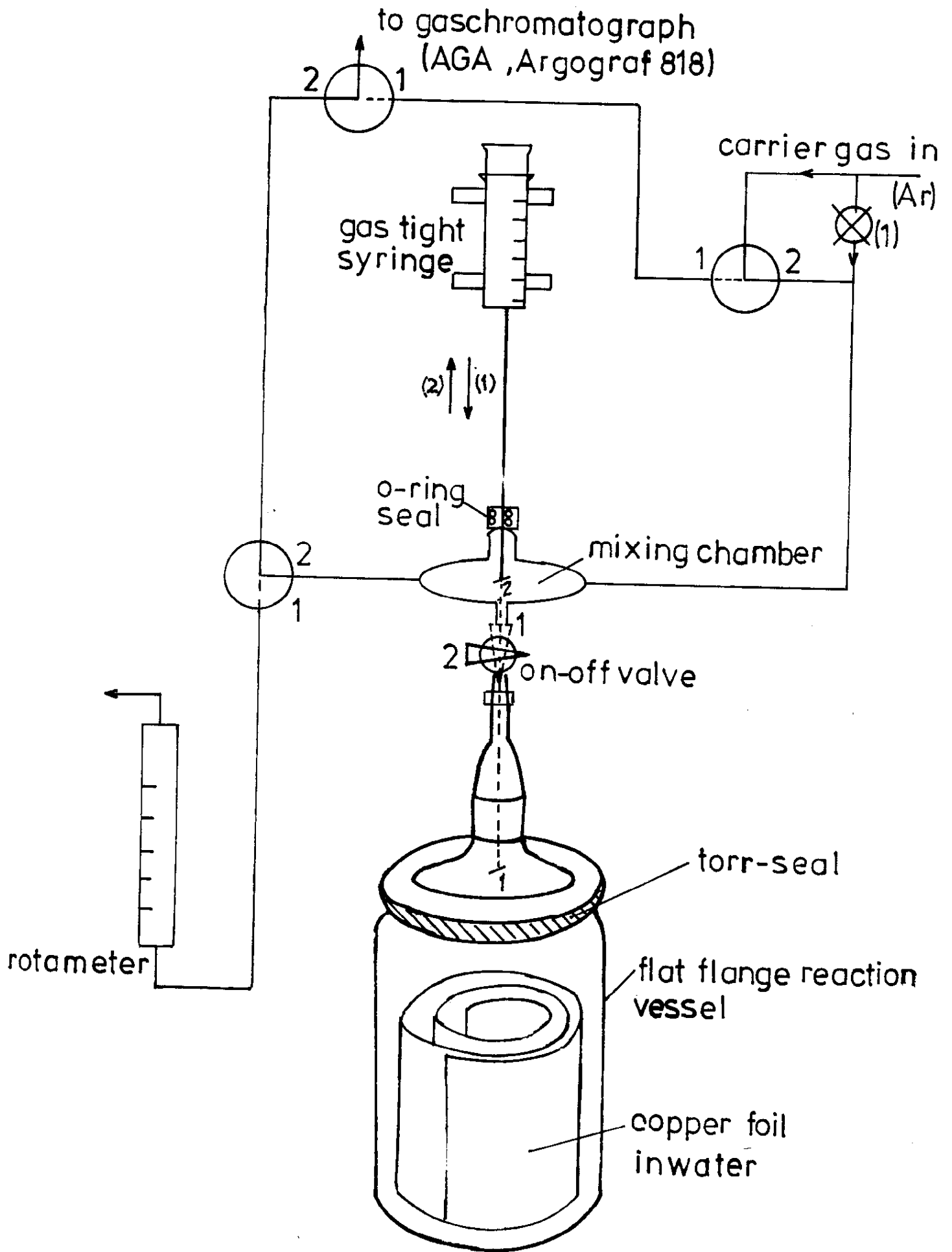


Fig 1: Schematic of reaction vessel and gas sampling system.

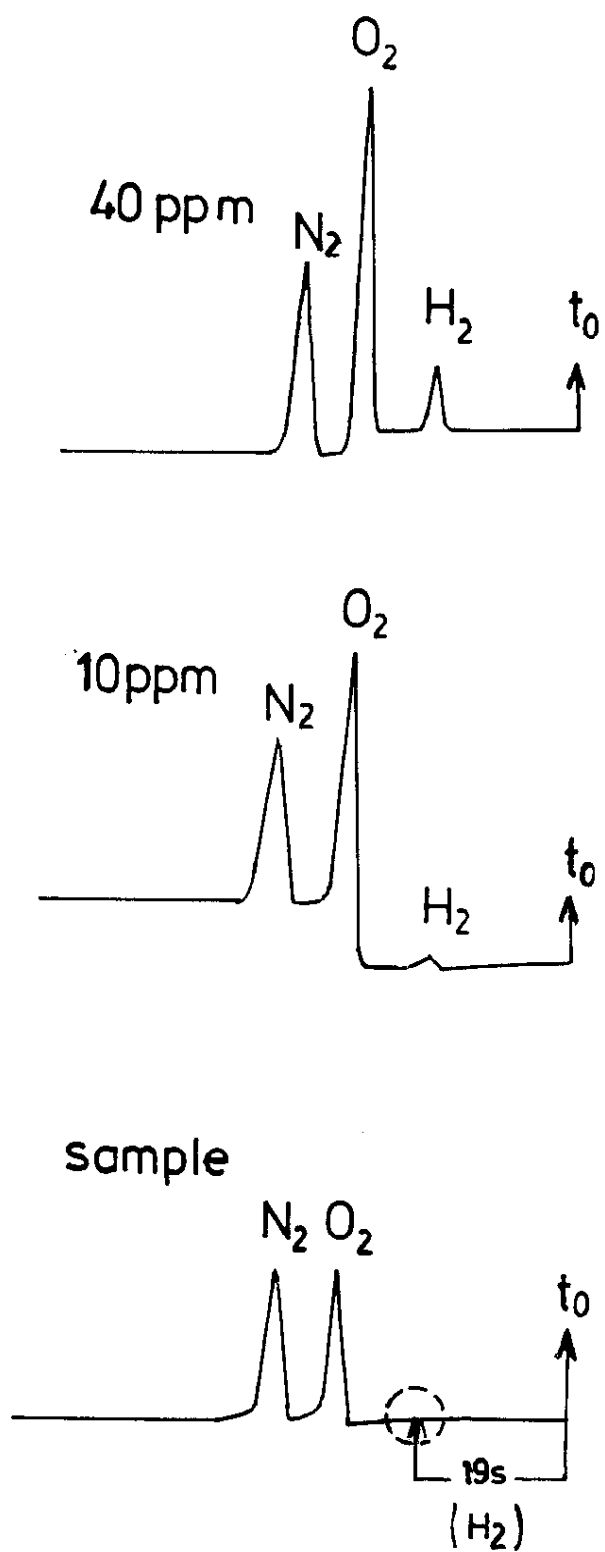


Fig 2: Chromatograms for gas phase samples from reaction vessel 720 h after start of experiment and reference gas mixtures containing 10 and 40 ppmv respectively.

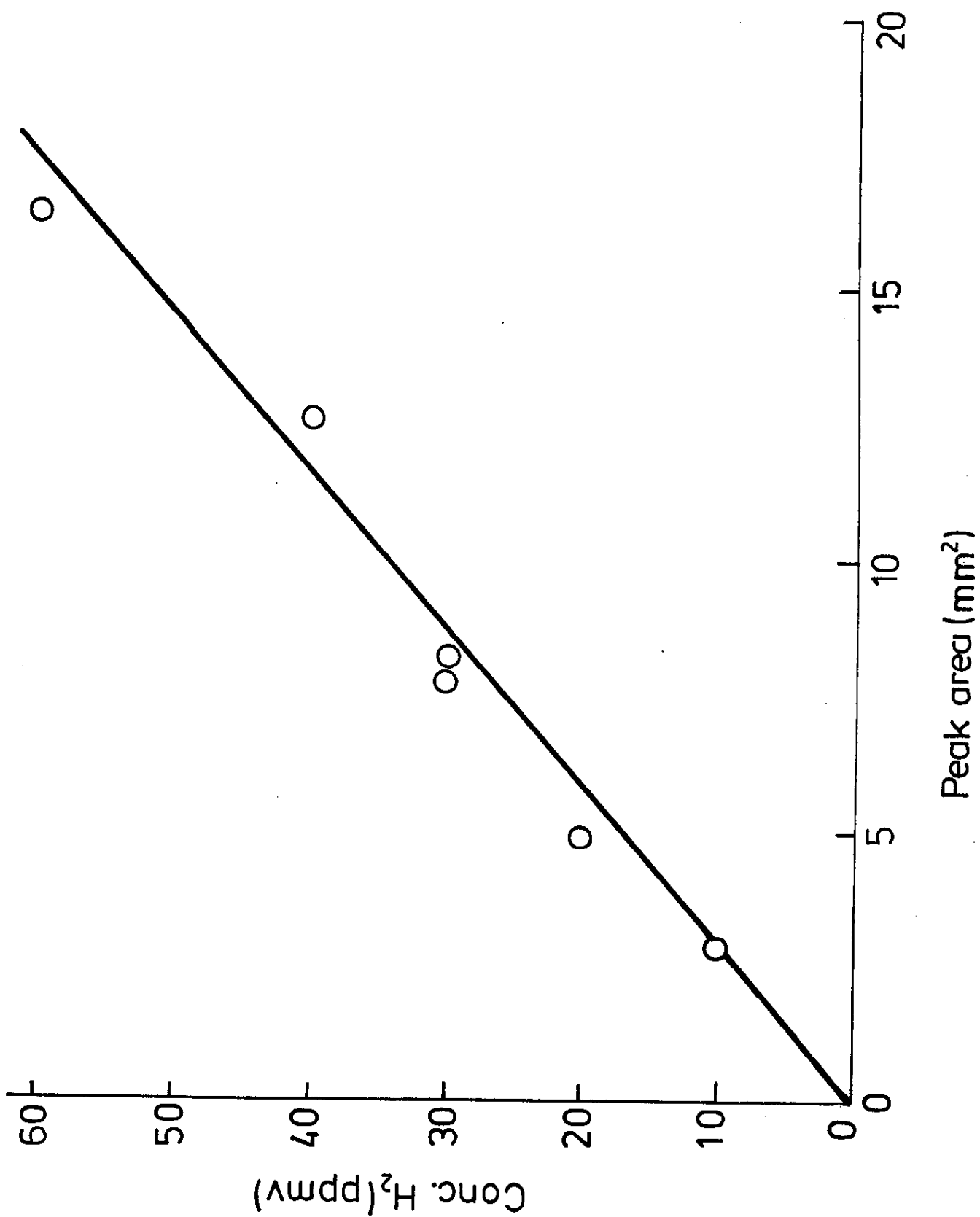


Fig 3: Calibration curve for gas sampling system.

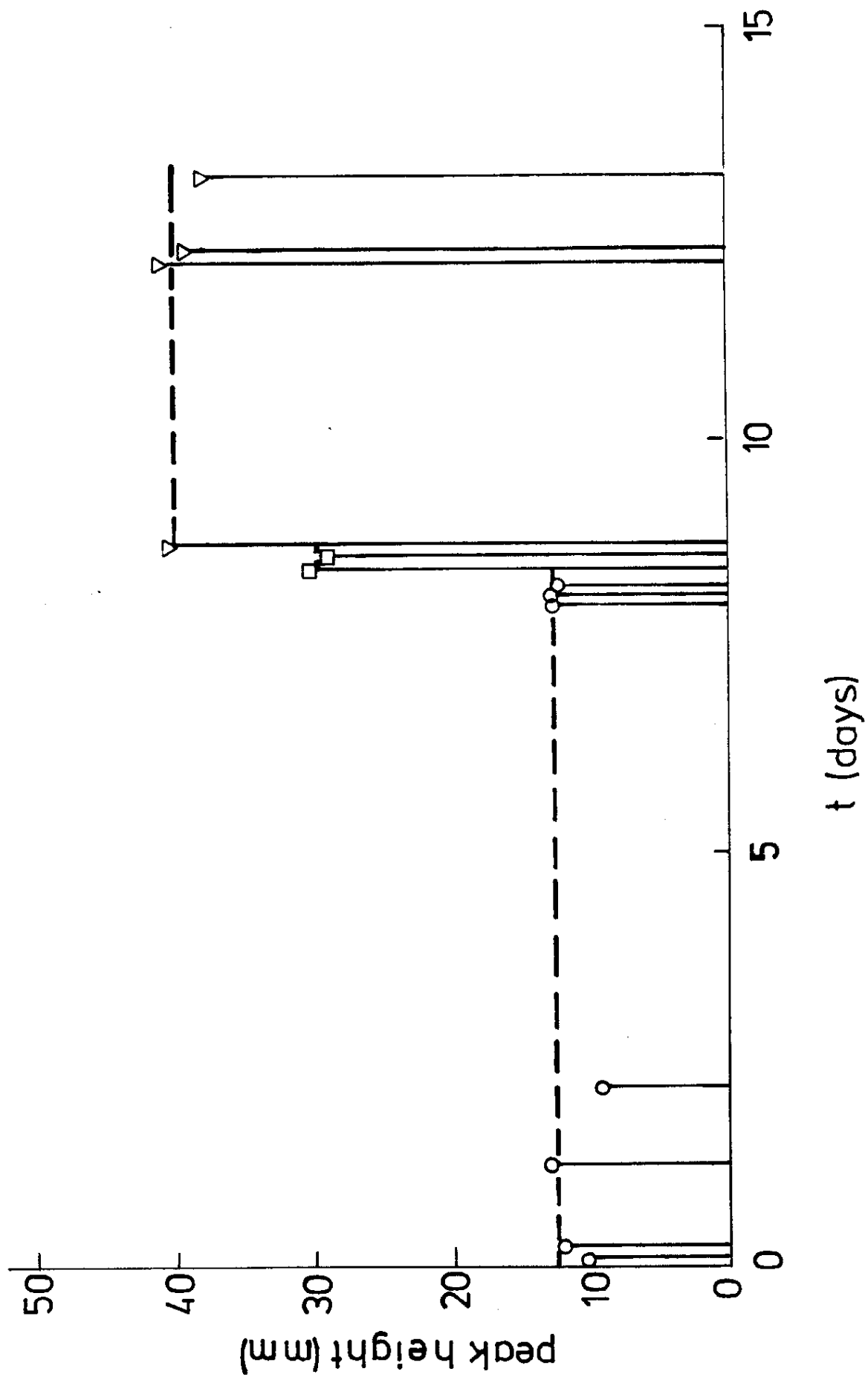


Fig 4: Height of H₂ peak in gas chromatogram versus time plot. H₂ was added to the reaction vessel at three different.

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Thomas Ittner¹, Börje Torstenfelt¹, Bert Allard²

¹Chalmers University of Technology

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