DETERMINATION OF THE HYDROGEN CONTENT OF FUEL ELEMENTS

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ABSTRACT

A new method and apparatus are reported for determination of the total hydrogen content by measurements on as-manufactured fuel elements, heated at prescribed temperature values between 200°C and 600°C.

The method is based on the catalytic oxidation of the organic compounds and transformation of the hydrogen in the equivalent water quantity which is analysed by a special infrared detector.

Different types of measurements for determination of the hydrogen content from graphite coating, UO_2 pellets and filling gas are presented.

Also, experimental observation regarding water release and graphite thermal decomposition kinetic are discussed.

1. INTRODUCTION

Due the major effect of the hydrogen on the structural integrity of zirconium alloys, determination of the total hydrogen content in the as-manufactured fuel elements, is of an essential importance.

The are three main sources of hydrogen in the fuel element [1]:

1°) from the UO_2 pellets;
2°) from the graphite layer;
3°) from the zircalloy sheath.

The hydrogen content of the UO_2 pellets is usually determinated by extraction in carrier gas at high temperature (minimum 1600°C) followed by analysis with thermal conductivity cells (e.g., LECO-type analyzer).

Also, determination of the hydrogen content of zircalloy sheaths is part of reception quality control, by similar gas extraction method.

Determination of the hydrogen content of the graphite layer is made by various methods, but many of them are based on the catalytic oxidation of the organic compounds contained in the graphite layer; in this way, the hydrogen is completely transformed in water, which are analysed by different techniques.

These methods, based on catalytic oxidation, differ by the type of sample (small sheath ring, scraped graphite) or by the type of the resulting water analysis (electrolytic cell, gravimetric/piezoelectric cell) [2].

The DCH-ME apparatus, which is presented in this paper, has two specific characteristics:

(1) the samples for analysis are **as-manufactured fuel elements**;

(2) the hydrogen equivalent water resulting from catalytic oxidation is analysed by a sensitive infrared detector.

Thus, the DCH-ME analyzer permits to determine the total amount of hydrogen from:

- the graphite layer;
- the moisture contained in the open porosity of the UO_2 pellets and in the filling gas.

The DCH-ME apparatus was completely designed and constructed by Ultraacoustics R&D Laboratory of the Institute for Nuclear Research - Pitesti / ROMANIA, and is now currently used for determination of the fuel hydrogen content in the QA System of the Nuclear Fuel Plant - Pitesti / ROMANIA.

2. METHOD AND APPARATUS

There are four main sequences in our measurement method for the hydrogen content determination [3]:

(1) Tight perforation of the end-caps of the fuel element and stabilisation of the carrier gas flow (helium).

(2) Fast heating of the fuel element sheath, at a prescribed temperature between 200°C and 600°C. As a result, the organic compounds from the graphite layer are decomposed/ sublimated and are taked by the carrier gas.

(3) Catalytic oxidation of the sublimated organic compounds and hydrogen released from the fuel element, in an oxidation furnace. The used catalyser is CuO, the catalytic reaction being supplied by O_2 injected in the carrier gas. In this was, at the end of the oxidation furnace, the carrier gas will transport H_2O vapours, CO_2 and O_2. The optimum temperature range is between 800°C and 950°C.

(4) Infrared analysis of the water content of the carrier gas. To perform this, a special differential cell with Lead Sulphide (PbS) photoresistances are used. The spectral range of this detectors is limited in the near - infrared region, by using Ge filters. In this way, the spectral response of the PbS photoresistances is comprised between 1.5μm and 3.5μm, with maximum sensitivity at around 2.7μm (fig.3).

The detailed block - diagram of the DCH-ME apparatus is presented in fig.1. It is composed by the following main systems:

(1) **Gas circuits** with pressure and flow rate controllers, tight perforation device, catalytic oxidation furnace. In the measure part of the gas circuits there is, also, a 2-way chromatographical valve for injection of the gas samples (hydrogen) for calibration and verification.

(2) **Controllers for the temperature stabilisation** around the software prescribed values, for the purification furnaces, oxidation furnace and for the analysed fuel element. The

temperature sensors for the purification and oxidation electrical furnaces are platinum thermocouples. For the fuel element heating, because it is necessary to have a very fast temperature rise, we use an electronic near - infrared pyrometer. For the all four temperature controllers the command signal is furnished by the process computer on the basis of special proportional - integral regulation algorithms.

(3) **Differential infrared detector.** Is an essential part of the apparatus. Its bloc-diagram is presented in fig.2. As we have specified, the infrared sensitive elements are PbS photoconductive detectors with Ge filters. This type of sensors has the advantage of a very high sensitivity in the spectral range of a maximum interest for water vapours detection, as it can be seen from table 1. But, on the other hand, the PbS photoresistances are, also, very sensitive to the temperature variations of its support. Thus, for obtaining a sensitivity around 5μg H_2, it was necessary to perform a temperature stabilisation of the photoresistance support as good as ±0.02°C. To attain this very high temperature stability, we use two independent temperature controllers:

- the first (BTP) is a liquid circulator with a built - in temperature control unit which pass thermostatically controlled liquid through the bath of the second - stage controller; BTP can assure a precision of ±1°C over 2 hour periods;
- second (BTS) is, also, a liquid circulator, but it use a thermistor as temperature sensor. The command signal formed by the electronic block BTS - E is a fixed frequency, variable duty - cycle TTL signal, having the duty - cycle proportional with the temperature error.

The infrared sources (filaments) are made by NICROTHAL wire. The base-line stability of the infrared detector is, also, influenced by the regulation accuracy of the filament current. Using ANALOG-TO-DIGITAL AND DIGITAL-TO-ANALOG conversion channels with 12 bits resolution in the numerical regulation loop, it was possible to obtain an accuracy as good as ±0.07% for a current regulation range of ±10%.

In order to eliminate the detector response to the CO_2 content of the carrier gas, two CO_2 filled rooms, in serial connection are provided, between the infrared sources and the measuring/reference rooms; also, to avoid the water vapour condensation on the glass windows of the optical system, the measuring and reference rooms are heated to around 70°C.

(4) **Process interface computer**. This system assure the command, control and synchronization of all functional blocks of the apparatus. It assure, also, the automatic acquisition, processing and storage of the detector response curves and of the analysis parameters. The I /O signals operations are performed by a high performances interface with 12 bits resolution on the analog input and output channels, and 30 KHz A/D conversion speed.

The specific software support "ANALIZOR" was elaborated as a C^{++} program with specialized functional blocks structurated as distinct subroutines:

$F_1 \ldots F_5$: Numerical regulation loops for the process parameters
F_6 : Performing calibration or verification (with injection of hydrogen calibrated volumes)
F_7 : Display of the detector response curves and selection of the interval for integration
F_8 : Processing of the response curves and calculus of the hydrogen content.

The first operation for performing a hydrogen content analysis, is the **calibration** of the apparatus. For this, 3 different calibrated hydrogen volumes (usually, between 0.5ml and 6ml) must be injected in the carrier gas. From the corresponding response curves, the software support of the apparatus automatically compute the **(hydrogen amount)/(response**

curve area) ratio. The value of this ratio can be verified any time by injection of known calibrated hydrogen volumes.

The heating of the tube or fuel elements samples is made by Joule effect, and it is important to know the temperature distribution during the analysis process.

The time dependences of the external surface temperature, measured with an infrared electronic pyrometer during the normal heating cycle of an analysis process, are shown in fig.12(a) for an empty tube sample and in fig.12(b) for a fuel element sample. It can be seen that the prescribed temperature (550°C) was reached very fast in the case of the empty tube and relatively slowly in the case of the fuel element.

The radial temperature distributions **calculated** [6] in these two cases are shown in fig.10 for empty tubes and in fig.11 for fuel elements. The temperature differences between the inside and outside sheath surfaces is very small (less than 0.1°C) in the case of the empty tube, with or without graphite layer ([6],[7]).

The radial temperature drop is more significant in the case of a fuel element (around 30°C between pellet surface and outside sheath surface) but it cannot affect the thermal decomposition of the organic compounds from the graphite layer or the water release from the UO_2 pellets.

The heat transfer calculations in the reference [6] were performed with the ANSYS 4.0 code, for usual values of the materials constants.

3. EXPERIMENTAL RESULTS

Different kind of measurement were made in order to characterize the performance of the method and apparatus.

(1) Statistical parameters for repeated measurements on hydrogen calibrated volume samples

For a set of n=10 calibrated volume samples, each containing 1.5ml H_2 (or, equivalently, 135µg H_2) the mean of the measured values was 133µg with 1.5% relative error.

Also, for n=10 calibrated volume samples of 6ml H_2 (or, equivalently, 540µg H_2) the mean of the measured values was 530µg H_2 with a relative error of 2%.

Typical response curves for different quantities of hydrogen are shown in fig.4.

(2) Determination of hydrogen content of ethyl cellulose samples

This measurements are of a great interest, because ethyl cellulose is the binder for the DAG 154 graphite type.

Ethyl cellulose is a range of compounds depending on the extent of ethoxyl substitution in cellulose [4].

We have used the N-22 compound from Acheson Colloids (sample GP31345, lot 713-2) with an assumed (calculated) hydrogen content of 8.6% [5].

The ethyl cellulose samples was preparated by deposition of 50µl-80µl of solution, on aluminium foil support. Then, the samples was heated at 200°C, around 20 min, for drying-off the solvent. A number of samples deposition on zircaloy-4 sheath support was, also, preparated, in order to verify the influence of the support nature.

The quantity of ethyl cellulose on each sample was determinated by gravimetric measurements.

The obtained results are shown in tables 2 and 3. Two sets of measurements are presented. In all cases, the estimated hydrogen content (calculated with the 8.6% assumed content) was in good agreement with the measured values.

No significant differences between the Al foil support and zircaloy-4 support can be noted.

For performing these measurements, the samples was introduced in an empty tube which is heated at 550°C in the normal process of the analysis.

Typical response curves for ethyl cellulose samples with different hydrogen content are shown in fig.5.

(3) Measurements on empty tubes, baked graphite

The obtained results are presented in table 4. Because the end-caps perforation was performed during the heating at 550°C, the determinated hydrogen content include, also, the filling gas moisture.

The analyzer response curve for the sample T_6 is shown in fig.6.

(4) Gradual thermal decomposition of unbaked graphite

An interesting experiment was performed on the tube sample T2G with unbaked graphite (helium filled). The amount of hydrogen relased in five thermal cycles at different temperatures was measured.

From the data presented in graphite layer is almost complete in the temperature range between 200°C and 250°C.

(5) Measurements on fuel elements

The hydrogen content of fuel elements with UO_2 pellets and baked graphite (helium filled) was measured in two thermal cycles at 200°C and respectively, 550°C. An inlet pressure of 4.5 atm was necessary in order to assure the normal flow rate (200ml/min) in the fuel elements, even at 200°C.

The obtained results are presented in table 6. An interesting feature appears in the response curve for the 200°C cycle (fig.7): the water from UO_2 pellets being the first released, its contribution is clearly separated from the graphite layer hydrogen content.

(6) Measurements on tube samples without graphite

A number of measurements was made on tube samples without graphite, air filled. The results (table 7) are very close on the estimated value of 110μg H_2 which correspond to the moisture from around $55cm^3$ of the samples, at 70% humidity.

Also, a measurement was made on a tube sample filled with Ar + 7% H_2 mixture (analysis temperature: 550°C). The determinated value is close to the calculated amount of hydrogen.

The corresponding response curve of the DCH-ME analyzer are presented in fig.8 and 9, respectively.

4. CONCLUSIONS

The new method and apparatus presented in the paper, permit the determination of the total amount of hydrogen from:

- the graphite layer

- the moisture contained in the open porosity of the UO_2 pellets and in the filling gas.

The apparatus (DCH-ME Analyzer) has the following specific characteristics:

(1) the samples for analysis are **as-manufactured fuel elements**;
(2) the hydrogen equivalent water resulting form catalytic oxidation is analysed by a very sensitive infrared detector;
(3) the temperature value of the sample during the analysis process can be prescribed in the range between 200°C and 600°C.

The accuracy of the hydrogen determinations is as good as 5%, demonstrated on calibrated hydrogen volume samples and, also, on ethyl cellulose samples.

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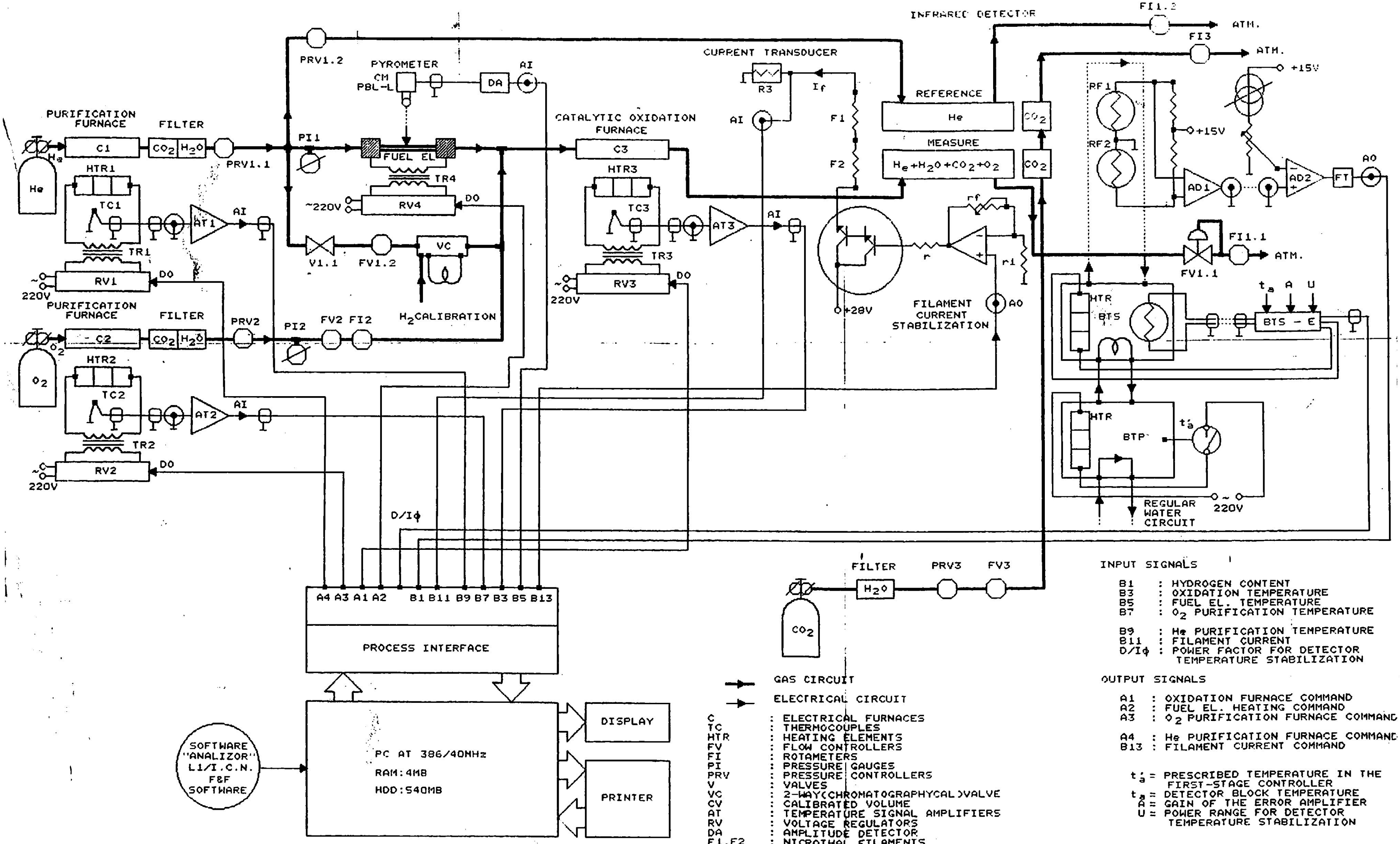


INPUT SIGNALS

B1 : HYDROGEN CONTENT
B3 : OXIDATION TEMPERATURE
B5 : FUEL EL. TEMPERATURE
B7 : O_2 PURIFICATION TEMPERATURE

B9 : He PURIFICATION TEMPERATURE
B11 : FILAMENT CURRENT
D/Iϕ : POWER FACTOR FOR DETECTOR TEMPERATURE STABILIZATION

OUTPUT SIGNALS

A1 : OXIDATION FURNACE COMMAND
A2 : FUEL EL. HEATING COMMAND
A3 : O_2 PURIFICATION FURNACE COMMAND

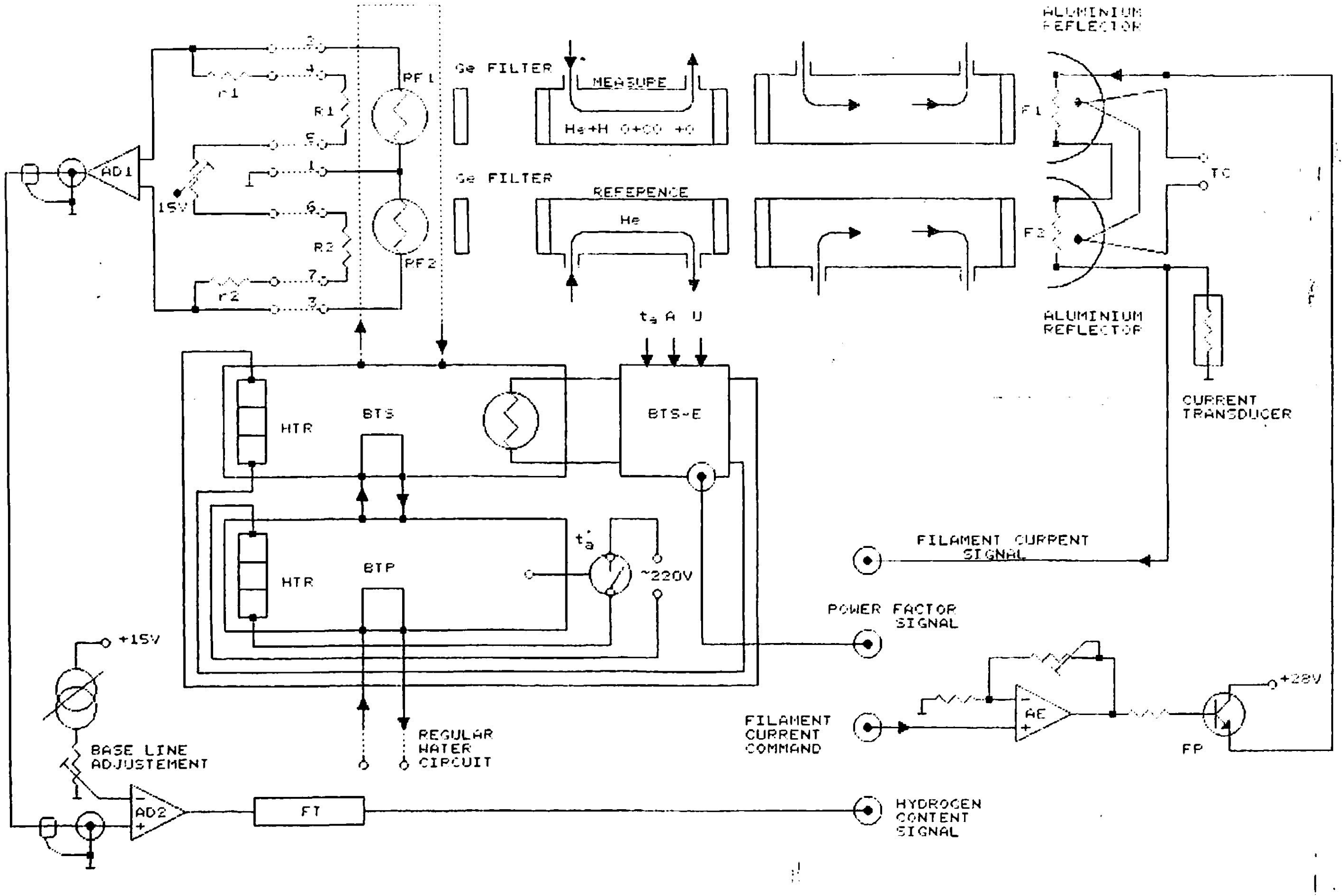
A4 : He PURIFICATION FURNACE COMMAND
B13 : FILAMENT CURRENT COMMAND

t_a' = PRESCRIBED TEMPERATURE IN THE FIRST-STAGE CONTROLLER
t_a = DETECTOR BLOCK TEMPERATURE
A = GAIN OF THE ERROR AMPLIFIER
U = POWER RANGE FOR DETECTOR TEMPERATURE STABILIZATION

→ GAS CIRCUIT
→ ELECTRICAL CIRCUIT

C : ELECTRICAL FURNACES
TC : THERMOCOUPLES
HTR : HEATING ELEMENTS
FV : FLOW CONTROLLERS
FI : ROTAMETERS
PI : PRESSURE GAUGES
PRV : PRESSURE CONTROLLERS
V : VALVES
VC : 2-WAY(CHROMATOGRAPHYCAL)VALVE
CV : CALIBRATED VOLUME
AT : TEMPERATURE SIGNAL AMPLIFIERS
RV : VOLTAGE REGULATORS
DA : AMPLITUDE DETECTOR
F1,F2 : NICROTHAL FILAMENTS
RF1,RF2 : PbS INFRARED PHOTORESISTANCES
AD : DIFFERENTIAL AMPLIFIERS
FT : LOW PASS FILTER
BTP : FIRST-STAGE TEMPERATURE CONTROLLER
BTS : SECOND-STAGE TEMPERATURE CONTROLLER
BTS-E : ELECTRONIC BLOCK OF BTS
TH : THERMISTOR

FIG.1 BLOCK - DIAGRAM OF THE DCH - ME APPARATUS



PF1,PF2 : LEAD SULFHIDE (PbS) FOTORESISTANCES
F1,F2 : NICROTHAL FILAMENTS
TC : Fe - CONSTANTAN DIFFERENTIAL THERMOCUPLE
AD1 : DIFFERENTIAL PREAMPLIFIER
AD2 : DIFFERENTIAL AMPLIFIER
FT : LOW PASS FILTER
AE : ERROR AMPLIFIER
EP : POWER ELEMENT
HTR : HEATING ELEMENTS
BTP : FIRST - STAGE TEMPERATURE CONTROLLER
BTS : SECOND - STAGE TEMPERATURE CONTROLLER
BTS-E : ELECTRONIC BLOCK OF BTS

t'_a = PRESCRIBED TEMPERATURE IN THE FIRST - STAGE CONTROLLER
t_a = PRESCRIBED TEMPERATURE IN THE SECOND - STAGE CONTROLLER
A = GAIN OF THE ERROR AMPLIFIER
U = POWER RANGE FOR DETECTOR TEMPERATURE STABILIZATION

FIG.2 BLOCK - DIAGRAM OF THE INFRARED DETECTOR

TABLE 1. Main absorption bands for H_2O and CO_2. Absorptivity A is expressed in percents of the maximum value corresponding to the $\lambda \sim 2.8\mu m$ H_2O band

H_2O			CO_2		
λ[μm]	A[%]	Absorption character	λ[μm]	A[%]	Absorption character
0.94	7.81	narrow band	1.60	15.55	narrow band
1.12	13.64	narrow band	1.65	14.82	narrow band
1.33	40.83	wide band	1.98	34.85	narrow band
1.37	75.02		2.05	48.88	narrow band
1.44	40.58		2.10	21.84	narrow band
1.78	40.76	wide band	2.62	39.67	wide band
1.85	83.25		2.65	69.16	
1.93	40.48		2.78	39.14	
2.7	39.62	wide band	4.10	39.66	wide band
~ 2.8	100		4.25	90.91	
2.9	39.80		4.35	39.83	

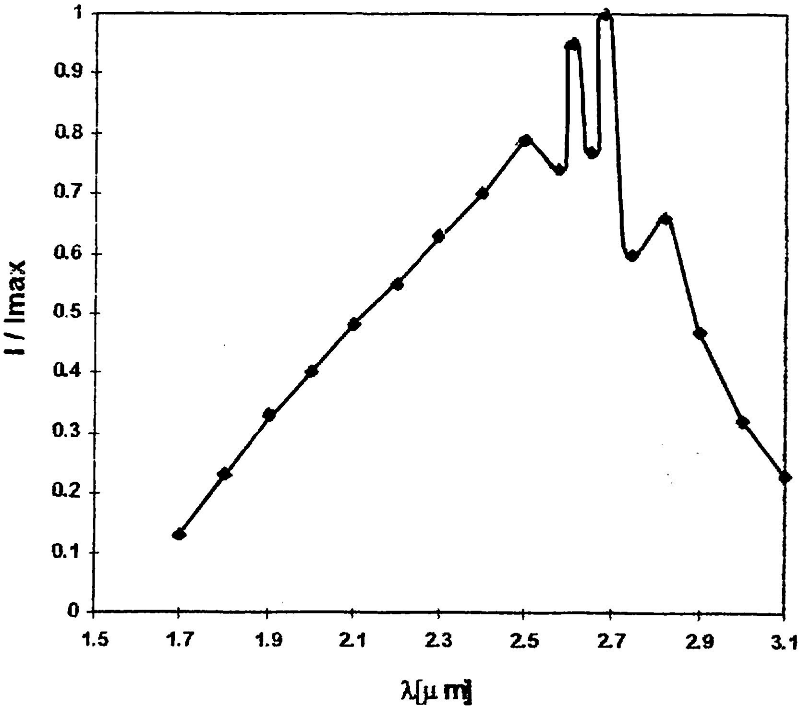
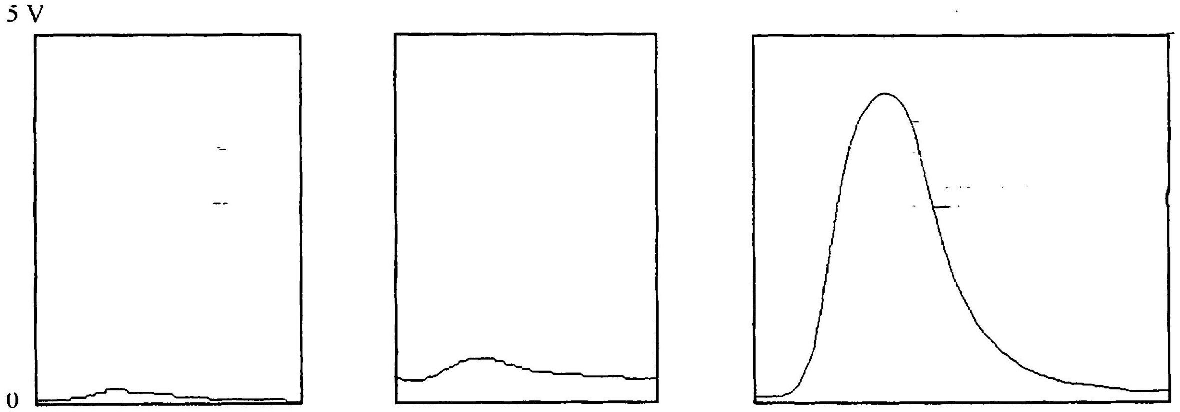


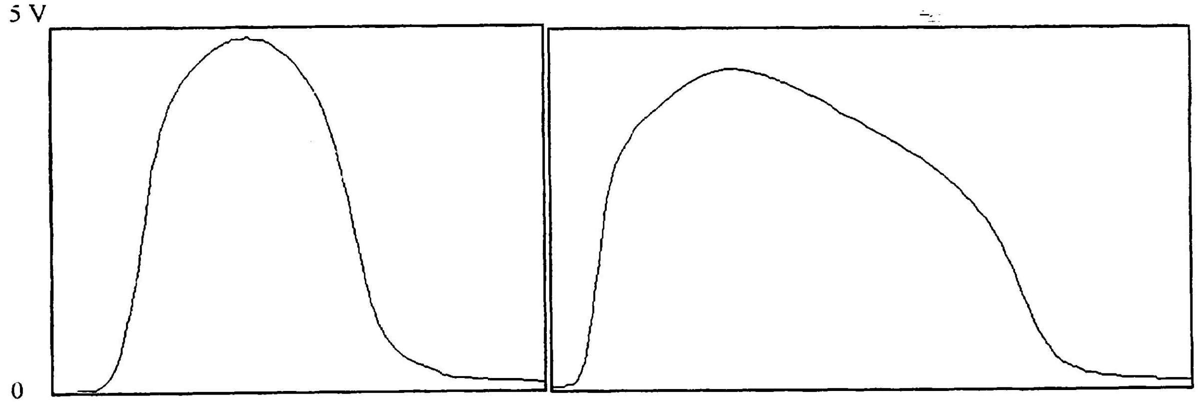
Fig.3. Spectral sensitivity of the PbS infrared photoresistances with Ge filters



Sample : 2,7μgH_2
Determinated : 4.8μgH_2
Analysis time : 19 s
Max. ampl. : 0.215 V

Sample : 9μgH_2
Determinated : 9.13μgH_2
Analysis time : 19 s
Max. ampl. : 0.608 V

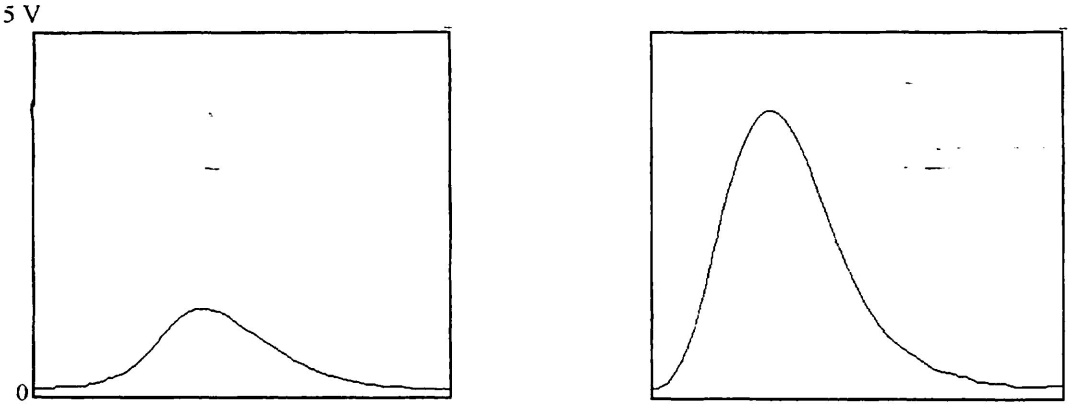
Sample : 135μgH_2
Determinated : 129.5μgH_2
Analysis time : 30 s
Max. ampl. : 4.216 V



Sample : 270μgH_2
Determinated : 250.2μH_2
Analysis time : 35 s
Max.ampl. : 4.863 V

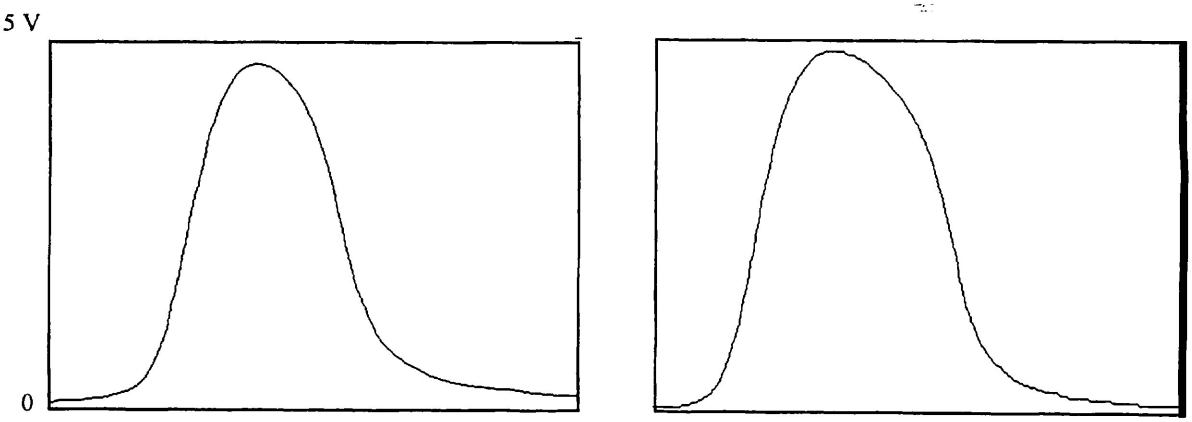
Sample : 540μgH_2
Determinated : 536μgH_2
Analysis time : 46 s
Max. ampl. : 4.44 V

Fig. 4. Analyzer response to different quantities of hydrogen.



Estimated content : 39 μg H_2
Determinated content : 45.7 μg H_2
Analysis time : 30 s
Max. ampl. : 1.243 V

Estimated content : 151 μg H_2
Determinated content : 161 μg H_2
Analysis time : 30 s
Max. ampl. : 3.945 V



Estimated content : 231 μg H_2
Determinated content : 228.1 μg H_2
Analysis time : 38 s
Max. ampl. : 4.692 V

Estimated content : 287 μg H_2
Determinated content : 292.2 μg H_2
Analysis time : 38 s
Max. ampl. : 4.919 V

Fig. 5. Analyzer response for ethyl cellulose samples with different hydrogen content.

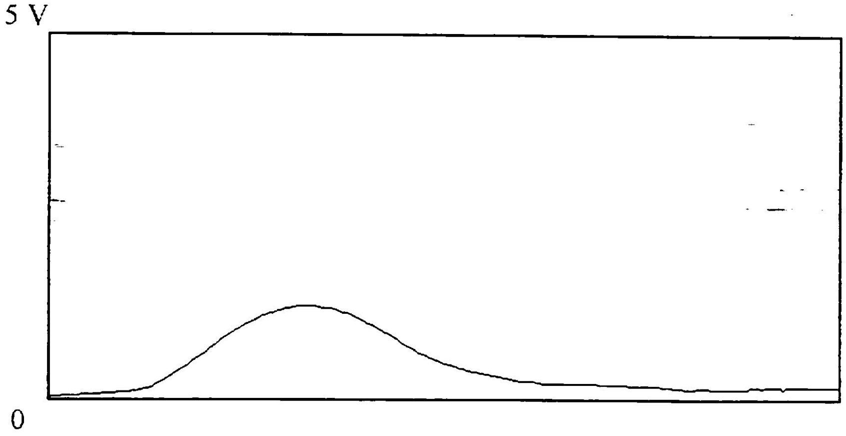


Fig. 6. Analyzer typical response for measurements on empty tube samples with baked graphite.

MEASUREMENTS PARAMETERS:

Sample code : T6
Analysis temperature : 550 °C
Flow rate : 200 ml/min
Analysis time : 57 s
Max. ampl. : 1.338 V
Determinated content : 84.5 µg H_2

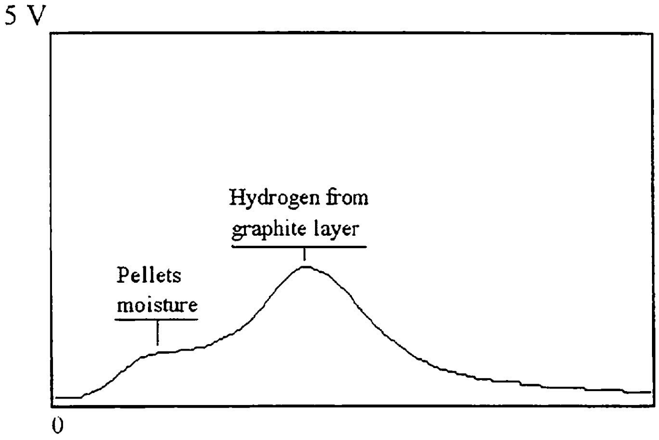


Fig. 7. Analyzer typical response for measurements on fuel element samples (with UO_2 pellets, baked graphite,helium filled) at 200 °C analysis temperature.

MEASUREMENTS PARAMETERS:

Sample code : EC 18
Flow rate : 200 ml/min
Analysis time : 44 s
Max. ampl. : 1.863 V
Determinated content : 88.1 µg H_2

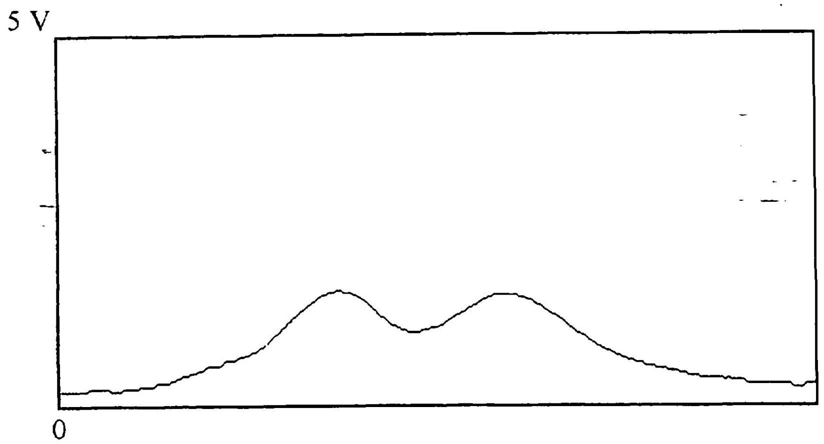


Fig. 8. Analyzer response for the measurement on the NG.AER 2 sample(tube without graphite, air filled).Estimated hydrogen content :110 μg.

MEASUREMENTS PARAMETERS:

Analysis temperature : 550 ^{0}C
Flow rate : 200 ml/min
Analysis time : 55 s
Max. ampl. : 1.577 V
Determinated content : 106.9 μg H_2

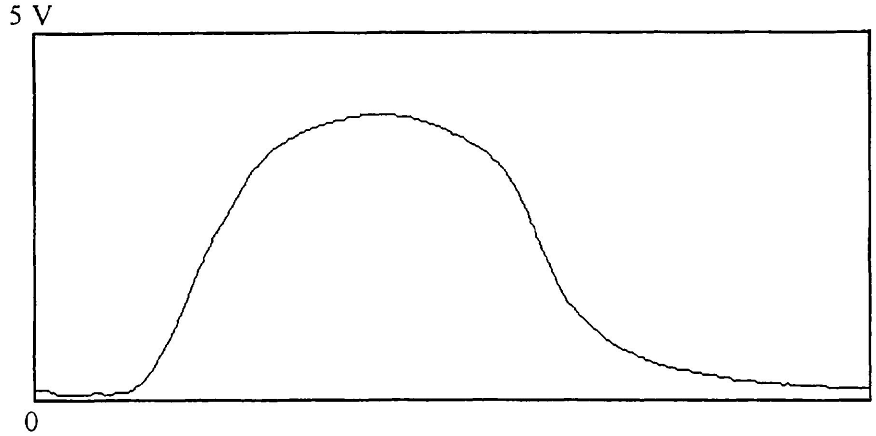
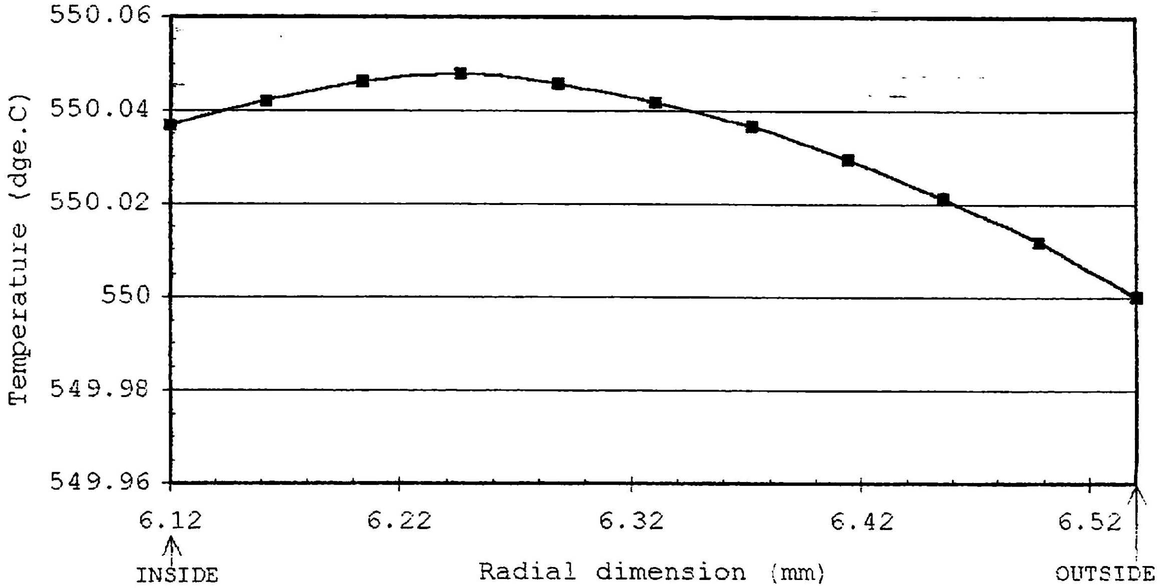


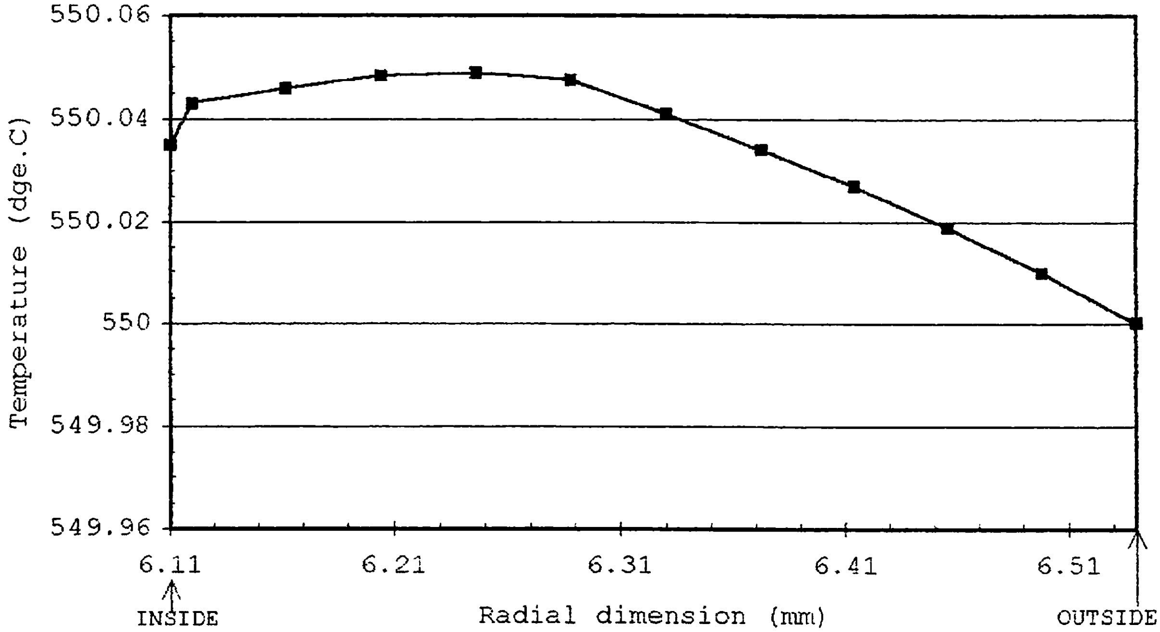
Fig. 9. Analyzer response for the measurement on the NGFZAH.72 sample (tube without graphite , filled with A_r +7%H_2 mixture).Estimated hydrogen content: 346 μg.

MEASUREMENTS PARAMETERS:

Analysis temperature : 550 ^{0}C
Flow rate : 200 ml/min
Analysis time : 60 s
Max. ampl. : 3.911 V
Determinated content : 371.9 μg H_2

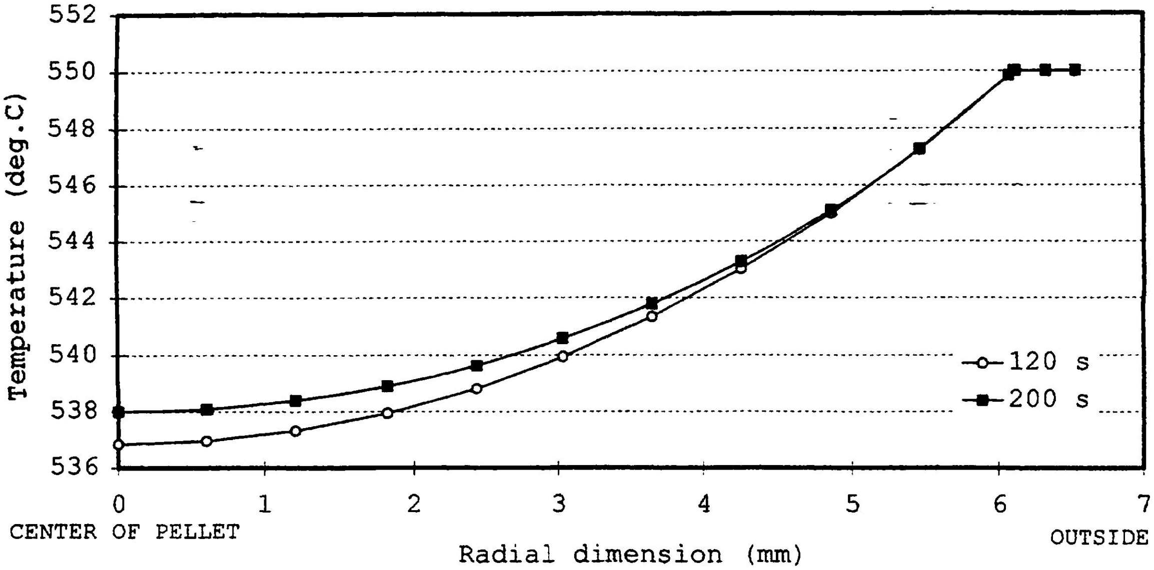


(a) Empty tube without graphite

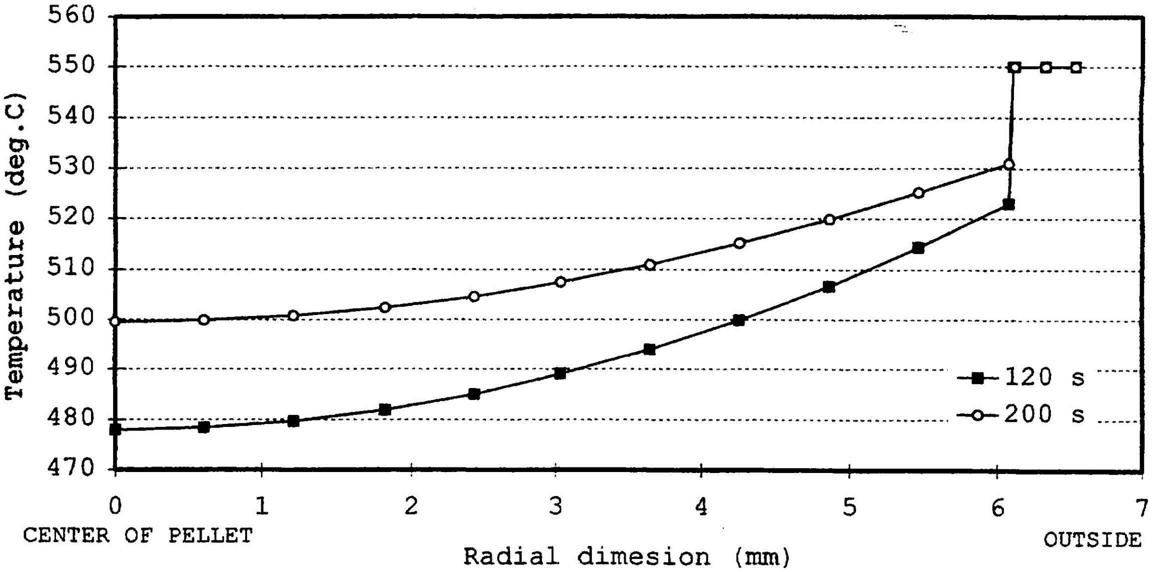


(b) empty tube with 10 μm graphite layer

Fig. 10. Calculated temperature distributions in the wall of a empty tube, during the hydrogen analysis thermal transient at 200 s after analysis strat-up

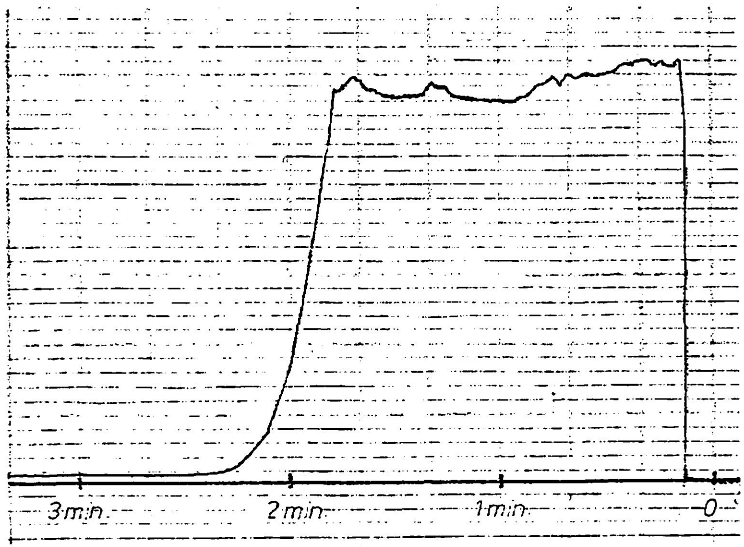


(a) fuel element with zero radial gap

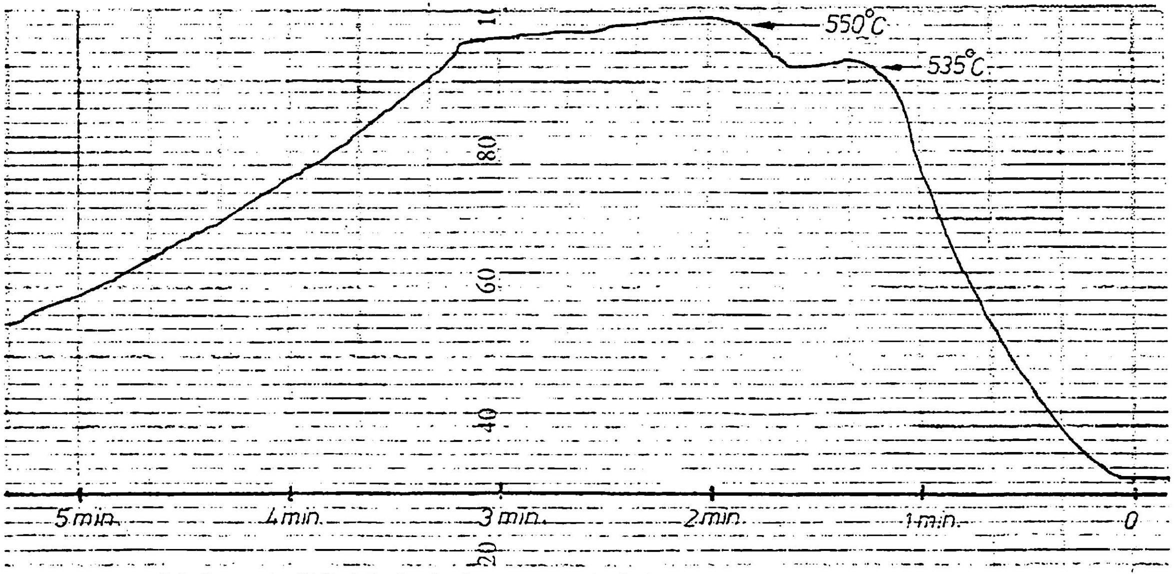


(b) fuel element with 0.05 mm radial gap

Fig. 11. Calculated radial temperature distribution in the fuel element, during the hydrogen analysis thermal transient at 120 s (o) and 200s (■) after analysis start-up



(a) Sample T$_7$: helium filled and normally graphitised



(b) Sample EC 16: fuel element with UO$_2$ pellets and baked graphite, helium filled

Fig.12. External surface temperature vs. time during hydrogen analysis, measured on:
(a) empty tube;
(b) fuel element.

TABLE 2. Analysis of ethyl cellulose samples deposited on Al foil.
Analysis temperature: 550°C
Date of analysis: July, 1994

Sample No	Estimated content of hydrogen [μg]	Determined content of hydrogen [μg]	Relative error [%]
1	231	228	1.3
2	304	300	1.3
3	270	287	6.3
4	271	279	2.9
5	287	292	1.7
6	287	283	1.4
7	143	160	11.9
8	151	161	6.6
9	142	153	7.7
10	165	182	10.3
11	152	150	1.3
12	154	164	6.5
13	134	139	3.7
14	165	162	1.8
15	155	149	3.9

TABLE 3. Results for ethyl cellulose samples, obtained at the yearly requalification test of the DCH-ME equipment. Analysis temperature:550°C.
Date of analysis: September, 1995

3.1. Samples deposited on Al foil

Sample No	Estimated content of hydrogen [μg]	Determined content of hydrogen [μg]	Relative error [%]
1	141	116	21.5
2	148	132	12.1
3	141	111	27
4	148	134	10.4
5	187	188	0.5
6	232	222	4.5
7	211	192	9.9
8	194	181	7.2
9	247	229	7.9
10	221	223	0.9

3.2 Samples deposited on zircaloy-4 support.

Sample No	Estimated content of hydrogen [μg]	Determined content of hydrogen [μg]	Relative error [%]
1	109	105	3.8
2	128	122	4.9
3	122	96	27.1
4	118	101	16.8

TABLE 4. Measurements on empty tubes with baked graphite. The tubes was helium filled and normally graphitised. Analysis temperature: 550°C.

Sample code	T6	T7	T8	T9
Determinated hydrogen content [μg]	85	104	125	83

TABLE 5. Gradual thermal decomposition of unbaked graphite.
Sample code:T2G

Measurement sequence	Temperature °C	Total hydrogen released [μg]	Detector amplifier linear gain
1	180	14	8
2	230	1500 (over scale)	2
3	250	312	3
4	400	133	5
5	550	63	8

Total amount of hydrogen > 2022 μg

TABLE 6. Measurements on fuel elements with UO_2 pellets and baked graphite, helium filled.

Sample code	EC17	EC18	EC16
Hydrogen evolved at 200°C	101	88	104
Hydrogen evolved at 550°C	54	49	70
Total amount of hydrogen [μg]	155	137	174

TABLE 7.Measurements on the tube samples without graphite, air filled.
Analysis temperature: 550°C

Sample code	NG Air 1	NG Air 2	NG Air 3
Measured value of hydrogen content [μg]	129	107	126

TABLE 8. Measurements result for a tube sample filled with Ar + 7%H_2 mixture.

Sample code	NGFZAH.72
Estimated hydrogen content [μg]	346
Measured value [μg]	372