An ESR cavity for performing ultimate sensitive ESR spin concentration measurements up to 1300 K

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Abstract A modification of a Varian TE 104 dual sample cavity is described. With this modified cavity, sample temperatures of up to 1300 K are reached without loss in sensitivity. The performance of this cavity allows one to measure the temperature dependence of very weak broad ($\Delta H \simeq 1$ kG) ESR signals. Moreover, it is possible to carry out spin concentration measurements reliably. The ideas underlying this modification can be used in general for making type TE 104 or TE 102 cavities suitable for sensitive ESR measurements at high temperatures.

1 Introduction

It is sometimes necessary to have information on the temperature dependence of the ESR spectrum (e.g. intensity, line width and g value). Commercial ESR heating units for temperatures higher than 350°C are not available and several workers have been trying to make high temperature ESR heating devices (for survey see Poole 1967, Alger 1968). Some of these devices have reached temperatures of about 1300 K by placing heating wires inside the cavity. Most of the cavities described in the literature are not adaptable to commercial spectrometers, the attainable sensitivity being much too low, especially at high temperatures. They are also not suitable for accurate determination of the spin concentration. Moreover, when broad ($\Delta H \simeq 1$ kG) ESR signals of low intensity are observed, it is extremely difficult to keep baseline drift and DC offset to low values. Because of the reasons mentioned above, we have modified a copy of the Varian TE 104 cavity. Two heating systems will be described.

2 Construction of the TE 104 high temperature cavity

With the type TE 104 cavity the sample to be measured is placed in one channel of the cavity and the standard sample in the other. Each channel of the Varian dual sample TE 104 cavity has two opposite 'windows' which occupy the greater part of their walls. Each window is covered by a stainless steel plate (0·06 mm in thickness) which is pressed against the wall by a frame containing a 100 kHz field modulation

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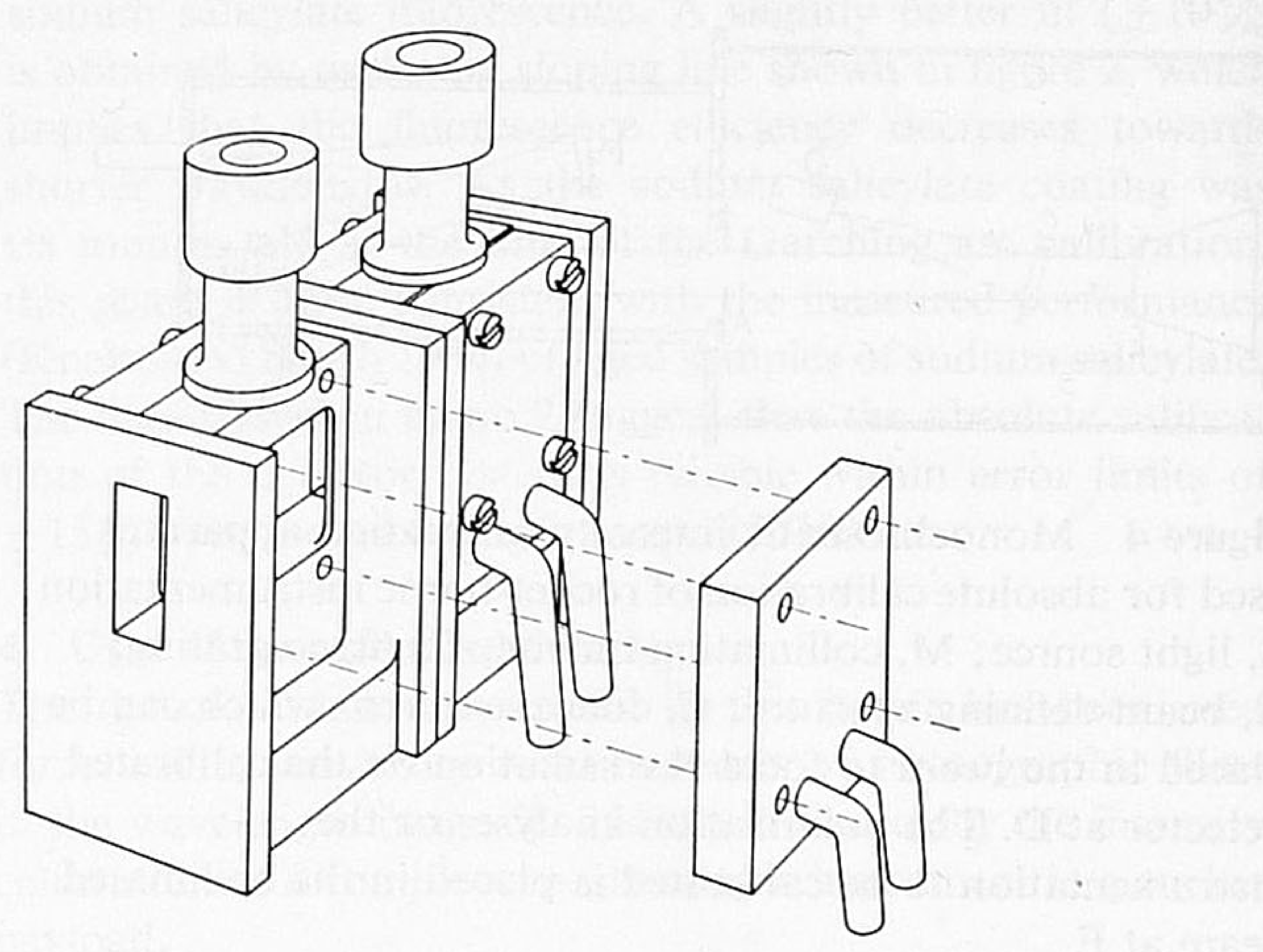

Figure 1 Exploded view of the laboratory made high temperature TE 104 cavity

coil embedded in Araldite. When the ESR sample, which is placed in a quartz dewar inside the cavity, is heated by a hot nitrogen gas stream, the cavity becomes hot. This in turn causes the quality factor to decrease, the measurements become irreproducible and baseline drift occurs. Effective cooling, which is necessary to do away with all these incompatibilities, is impracticable. In order to make possible sensitive and reliable spin intensity measurements at high temperatures (800°C) we have designed a new type of cover for the windows as described below.

In figure 1 an exploded view of the high temperature cavity is shown. Its body, made of brass, has the same dimensions as the Varian TE 104. A layer of approximately 2–5 μm of silver is applied electrolytically. To avoid oxidation of the silver layer, the body is electrolytically gold plated. This procedure ensures low skin depth (low losses) in the cavity walls. No glossing material is added to the baths, because this decreases the quality (Q) considerably, To ensure sensitive measurements at high temperatures, direct cooling of the covers was chosen. Moreover, it was not necessary to make provision for cooling the body of the cavity. Cooling of the new covers was sufficient for maintaining a high quality factor of the cavity at high temperatures.

Magnetic field modulation with a frequency of 10–100 kHz is necessary for a low noise level of the microwave detector. To avoid great losses of the modulation field inside the cavity, the thickness of the plate between the window and the modulation coil has to be small in comparison with the corresponding skin depth. Therefore, the Varian uses a stainless steel plate of about 0·06 mm thickness.

To ensure sensitive measurements at high temperatures the frequency and maximum amplitude of the magnetic field modulation should be the same as in the original cavity. The new covers consist of a Nichrome plate of 0·2 mm thickness silvered on the side facing the samples. The Nichrome plate is fitted to a cooling compartment in which the modulation coils are mounted.

A cross section of a cover with cooling compartment is shown in figure 2. Cooling water, entering through the inlet in the cover, produces a water flow passing between the Nichrome plate and the modulation coil. Due to the use of a 0·2 mm thick Nichrome plate the amplitude of the 100 kHz field modulation is decreased by a factor of 1.1, whereas the cooling and rigidity are satisfactory. The configuration of the modulation coils is nearly the same as in the original cavity,

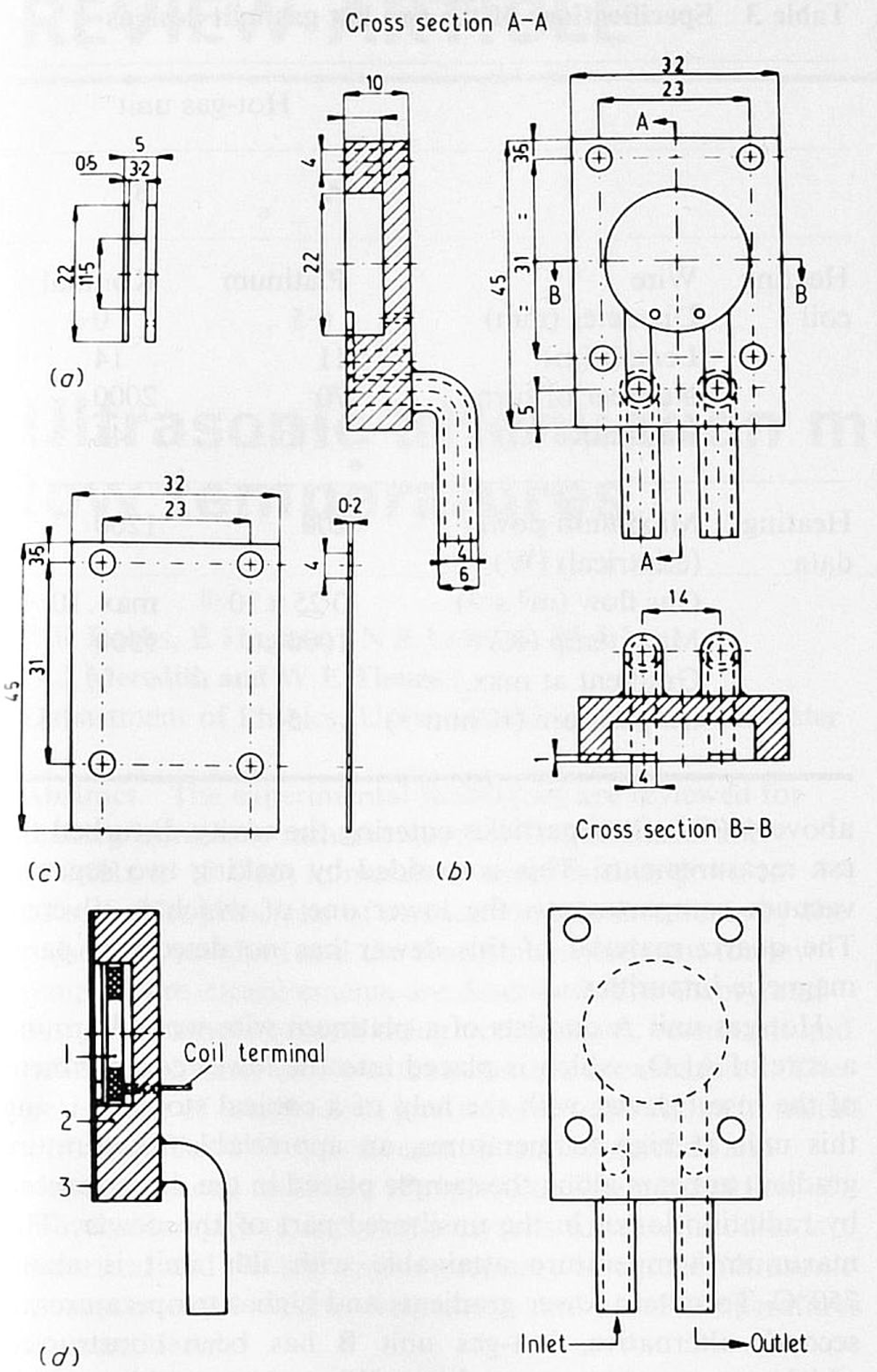

Figure 2 Cover with cooling compartment (all dimensions in mm). (*a*) Coil holder (perspex); (*b*) cooler (copper); (*c*) plate (Nichrome); (*d*) cover

although the impedance of the modulation coils has to be adapted to the 100 kHz modulation amplifier.

When mounting the covers directly on the cavity body, problems arise when ESR recordings of great sweep ranges are performed at high sensitivity settings, usually causing the baseline of the recorder to go off scale. It is our experience that silver gaskets between the silvered Nichrome plate and the cavity wall prevent this DC offset at great sweep ranges. The screws of the cooling compartments and the flange connection between the waveguide and the cavity have to be tightened with the same torque (6–14 lb in) in diagonal succession.

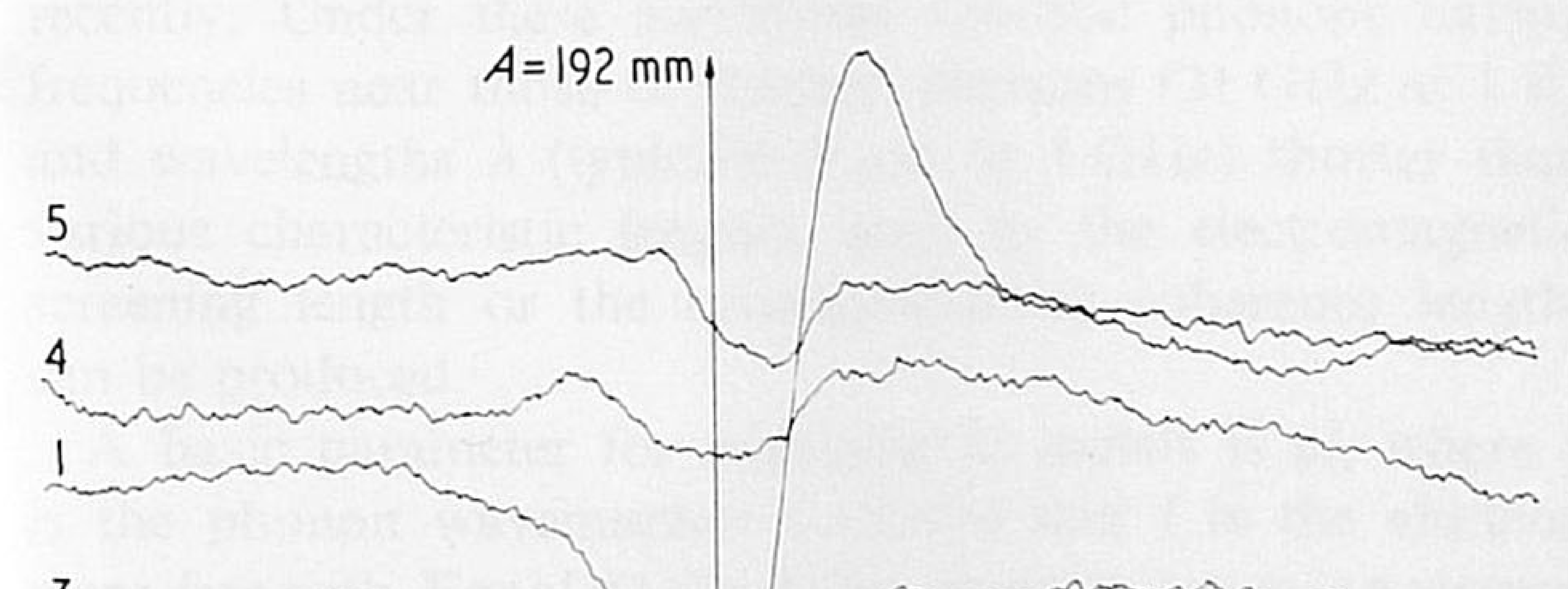

Figure 3 ESR test of the laboratory made high temperature TE 104 cavity. For specifications of scans 1 to 5 see table 1

Table 1 Experimental conditions and settings of the E-15 ESR spectrometer for scans 1–5 of figure 3

Measurement†	Varian weak pitch	Noise	DC offset		
Scan number	1	2	3	4	5
Temperature (°C)	20	20	20	20	650
Field set (G)	3269	1500	2500	2500	2500
Scan range (G)	40	0	2000	4000	4000
Scan time (min)	4	2	4	4	4

† All measurements were carried out in the same (heating) channel at a time constant of 1 s, receiver gain of 8×10^3, HF power of 160 mW, and with the modulation amplitude chosen for maximum signal height.

Table 2 Specifications of the laboratory made high temperature TE 104 cavity

Quality factor	Q_{loaded} 4000 (without dewars)	
	Q_{loaded} 4200 (with dewars)	
	Quality factor constant within 5% up to 1300 K	
Sensitivity	Test carried out in combination with Varian E-15 spectrometer	
	Test sample Varian weak pitch: 10^{13} spins in effective volume of cavity	
	Signal to noise ratio is $A/N\times2{\cdot}5\simeq100$ (method prescribed by Varian)	
	Test sample placed in insert dewar	
	Insert dewar in other channel empty	
Offset baseline	25% of a weak pitch	
Flow cooling water	1 ml s^{-1}	
Modulation coil (consists of 5 wires wound in parallel)	Coil holder	see figure 2
	Wire diameter	0·15 mm
	Length	5 m
	Number of turns	90
	Inner diameter coil	11·5 mm
	Outer diameter coil	20 mm
Electrical data of the coil	Impedance	40 Ω at 10^5 Hz ($\phi=82°$)
	DC resistance	0·8 Ω

When spin concentration measurements are performed a standard sample is placed in an insert dewar in the second channel. It is kept at a well defined temperature ($T=20°C$) with the aid of a gas flow.

An ESR test and the specifications of the high temperature ESR cavity are given in figure 3 and table 2 respectively. When using the original Varian cavity at temperatures higher than 400°C with the heating devices described, but without the new type of cooling cover, the quality factor of the cavity decreases and considerable instabilities occur. The measurements became irreproducible and large DC offset at great sweep ranges (>250 G) make sensitive measurements impossible.

The original Varian dual sample cavity can be used in combination with the new covers if the four screws holding the two cavity parts together are countersunk. Using rectangular cavities of other dimensions, the diameter of the modulation coil has to be adapted (Helmholtz configuration). For performing high temperature measurements on other ESR spectrometers the impedance of the modulation coil has to be matched to the output of the modulation amplifier.

3 Heating devices

Two possible methods for heating the sample inside the cavity were tried. They were the hot gas stream (HG) and the heating wire methods. The advantage of the heating wire method is the direct heating of the sample. However, the great sensitivity of the Q factor to the position of the wire, particularly in the TE 102 cavity, makes this method less desirable. Lorentz forces cause displacement of the wires inside the cavity when the static magnetic field is scanned. This produces short-term changes in the quality factor of the cavity, which results in irreproducible measurements. In general it is our experience that it is not suitable for sensitive ESR measurements. The hot gas method was therefore chosen in preference. For this, two heating devices have been developed which are extensions of the Varian hot gas stream method.

The two hot gas unit designs are shown in figure 4. The insert dewar is a modification of the Varian dewar (part no. 961–180). The unmodified dewar has a single vacuum compartment of which only the lower half is silvered to reduce radiation losses. It was found that at sample temperatures above 400°C silver particles entering the cavity disturbed the ESR measurements. This is avoided by making two separate vacuum compartments, the lower one of which is silvered. The quartz material of this dewar has no detectable paramagnetic impurities.

Hot-gas unit A consists of a platinum wire wound around a core of Al_2O_3 which is placed into the lower compartment of the insert dewar with the help of a conical stopper. Using this unit at high temperatures, an appreciable temperature gradient appears along the sample placed in the dewar caused by radiation losses in the unsilvered part of the dewar. The maximum temperature attainable with this unit is about 750°C. To obtain lower gradients and higher temperatures, a second, alternative, hot-gas unit B has been constructed which can produce more heat. When in use this unit is connected to the insert dewar. The technical specifications of the heating devices are given in table 3.

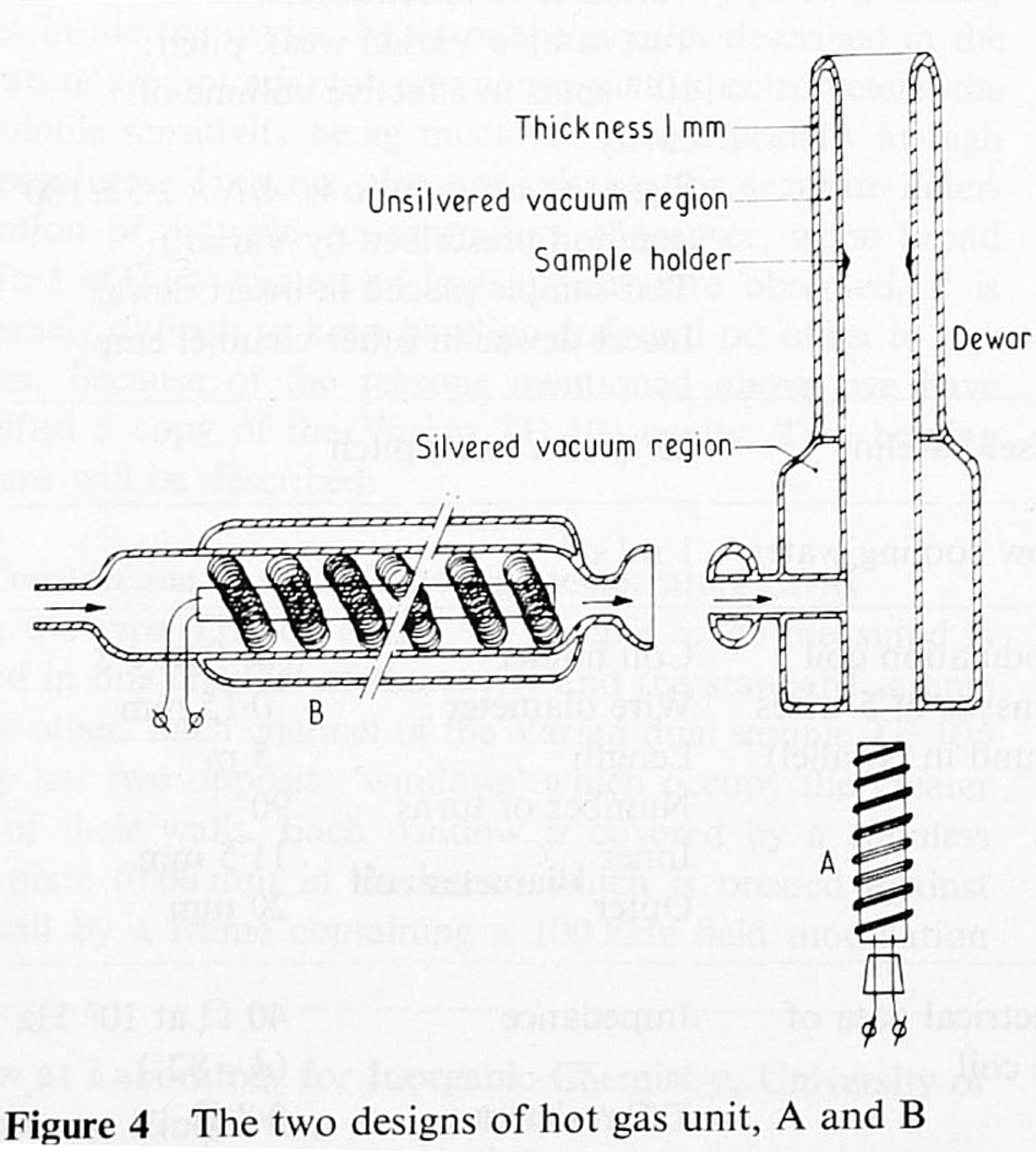

Figure 4 The two designs of hot gas unit, A and B

Table 3 Specifications of the two hot gas unit designs

		Hot-gas unit A	Hot-gas unit B
Heating coil	Wire	Platinum	Konthal
	Diameter (mm)	0·5	0·4
	Length (m)	11	14
	Number of turns	70	2000
	Resistance (Ω)	1 to 3	45
Heating data	Maximum power (electrical) (W)	200	1200
	Gas flow ($m^3 s^{-1}$)	$0·25\times10^{-3}$	max.10^{-3}
	Max. temp (K)	1000	1300
	Gradient at max. temperature ($K mm^{-1}$)	5	1·5

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