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**Supplementary Material**

# Flash (Vacuum) Pyrolysis Apparatus and Methods

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## Figures S1-S12: Additional drawings and photographs of pyrolysis equipment

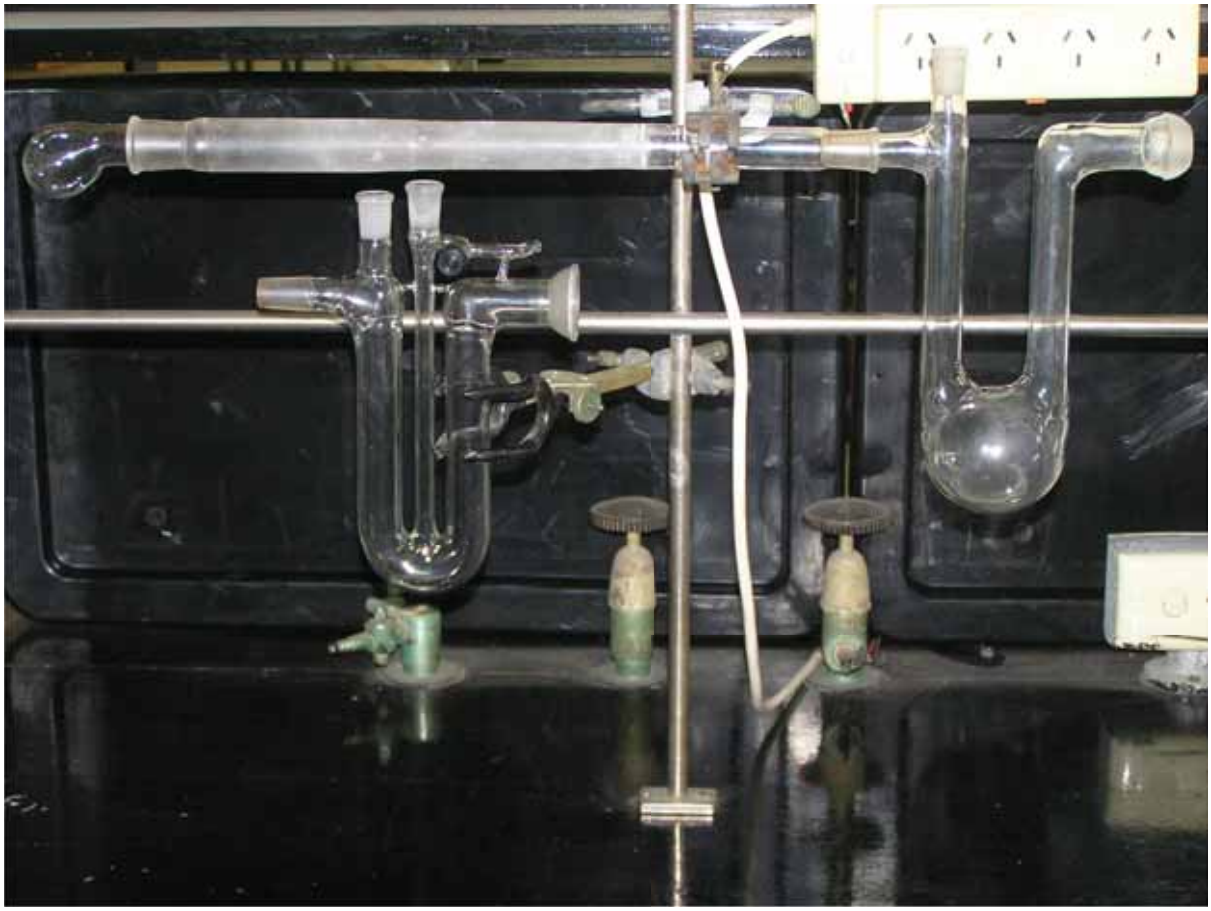

**Figure S1**. The quartz pyrolysis tube, sampe inlet tube and two different cold traps for the preparative FVP apparatus (for use with the ROK 3/30 oven in Figure 3b). Photo by the author.

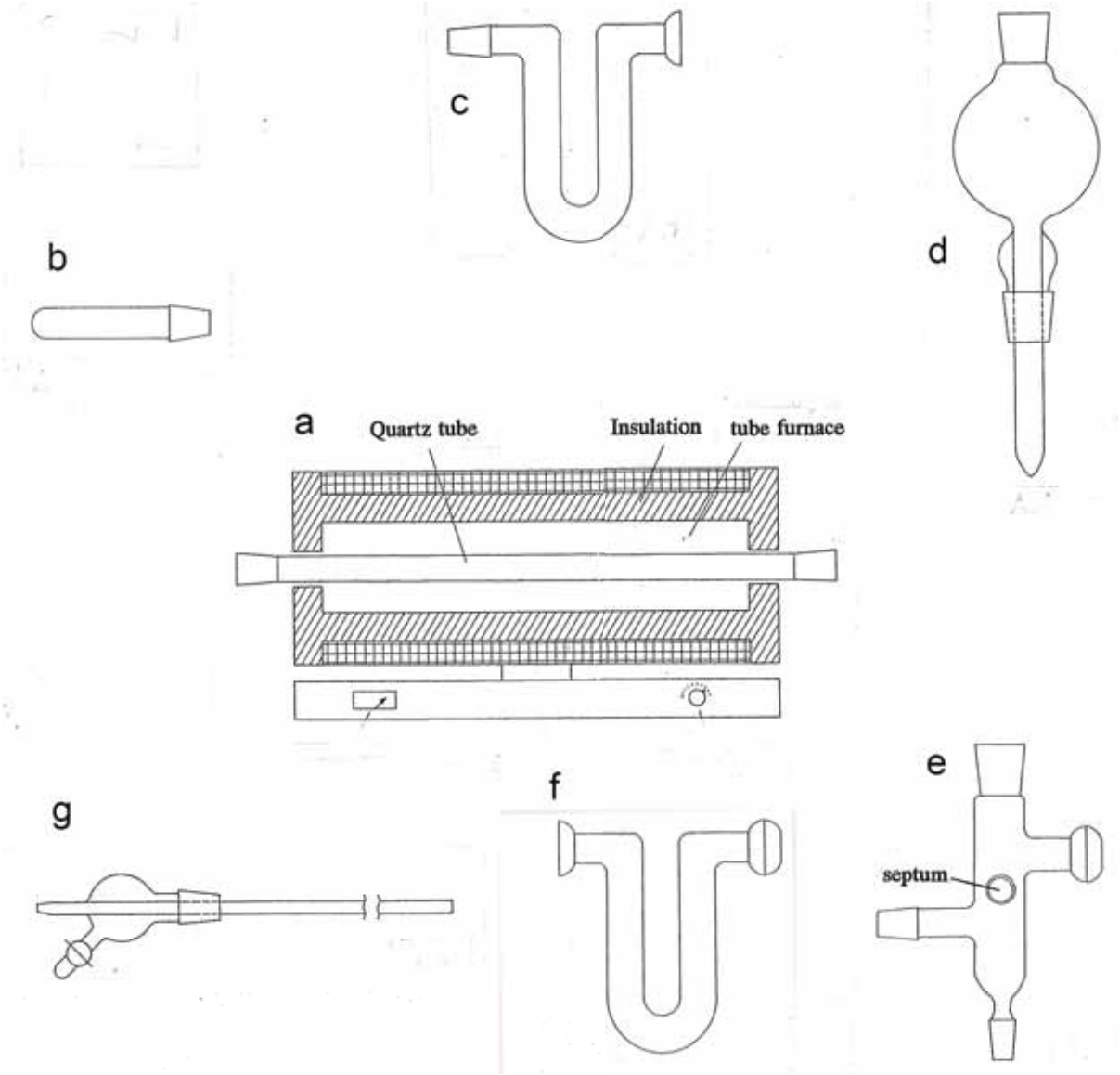


**Figure S2**. Accesories for preparative pyrolysis. (a) electrical tube furnace with quartz pyrolysis tube (usually 32 cm internal length, 2 cm I.D.), (b) sample tube, (c) U-tube cold trap, (d and e) cold finger with septum for injection of trapping agent or NMR solvent. (f) additional cold trap (may be required when volatile products are formed or when "hot trapping" with a volatile solvent, e.g. MeOH, is employed). (g) Inlet tube for gaseous trapping agent, e.g. MeOH/Ar, etc, going through the sample tube and terminating ca. 5 cm before the exit of the pyrolysis tube. Design by Rodney J. Blanch and C. Wentrup.


**Figure S3.** Schematic illustration of concentric tube trapping of reactive molecules (”hot trapping”). For example, the three individual ketenes in Figure S4 may be trapped, e.g. with MeOH. The inner, concentric, tube (2-4 mm I.D.) passes through the sample inlet tube and the pyrolysis tube (20 mm I.D.) and terminates near the end of the pyrolysis tube (the exact length can be varied) (see Figure S2). Ar or $N_2$ is used as a carrier gas to minimize back-streaming of trapped product. A premixed mixture of trapping agent and carrier gas is fed in through a needle valve or a capillary, or the trapping agent is entrained by he stream of carrier gas. For small scale work the mixture of trapped product and excess trapping agent is collected on the cold finger (77 K), and for larger scale work better in one or two consecutive cold traps.

A septum can be seen on the shroud of the cold finger. This is for injecting a trapping agent or a solution of it onto the pyrolyzate for “cold trapping”. A layer of trapping agent can also be deposited on the cold finger prior to the pyrolysis. The pyrolyzate is then sandwiched between two layers of trapping agent. After the end of the pyrolysis, pumping is interrupted, the liquid $N_2$ is blown out of the cold trap with gaseous $N_2$, the apparatus is partially filled with $N_2$ or Ar, and the cold finder is allowed to warm up. Thawing of the material will cause it to flow into a receiving flask below the cold finger. The same setup is used for injection of an NMR solvent on to the cold pyrolyzate, then allowing it to flow into a cooled NMR tube on thawing. Photo by the author.

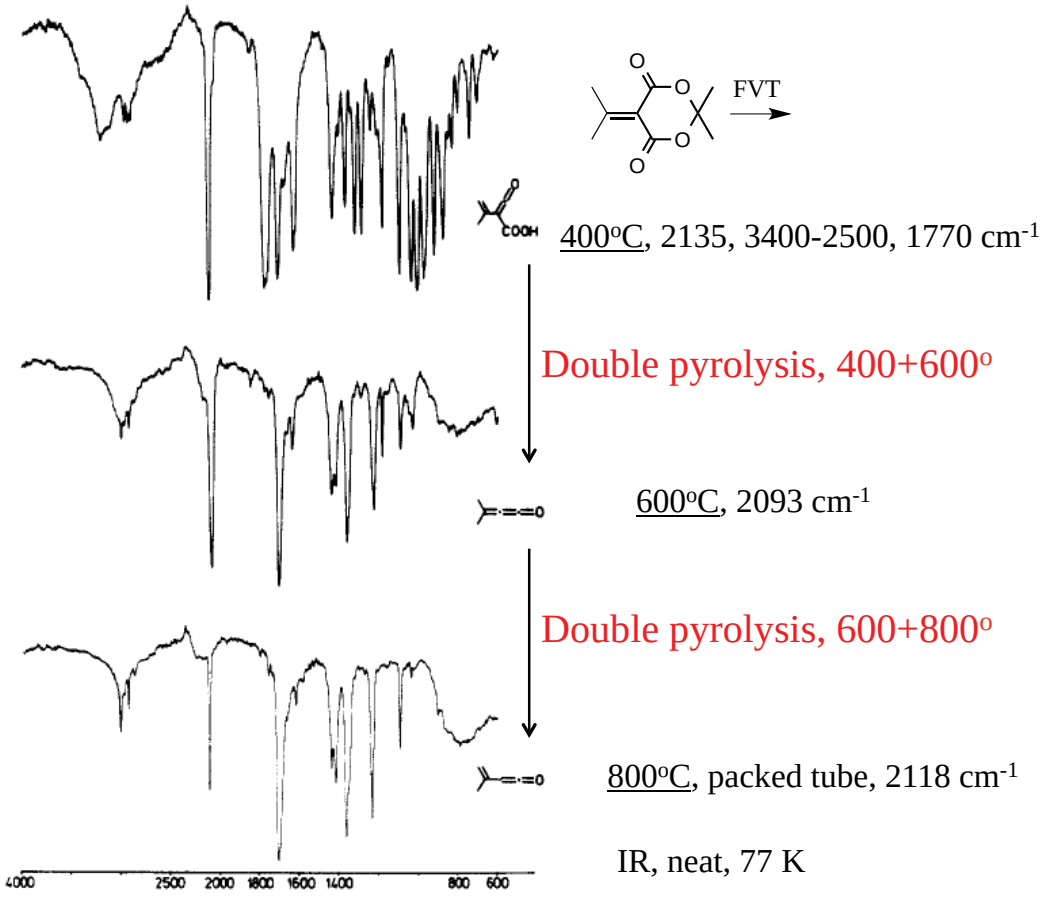


**Figure S4**. Double pyrolyses to illustrate sequential ketene formations. The apparatus in Figure 5 in the paper with two heating zones is used. The starting material is first pyrolyzed at one specific temperature, e.g. 400, 600, or 800°C, and the IR spectrum of the product condensed at 77 K is observed. Then double pyrolyses are performed with the two pyrolysis zones at 400 and 600°C, respectively, and another experiment with the two zones at 600 and 800°C. Moreover, the individual ketenes may be trapped, e.g. with MeOH, by using the apparatus shown in Figure 3a as illustrated in Figures S11 and S12. For details, see C. Wentrup, P. Lorencak, *J. Am. Chem. Soc.* **1988**, *110*, 1880.

**Figure S5**. A simplified version of the piptopysolysis apparatus. Photo by the author.

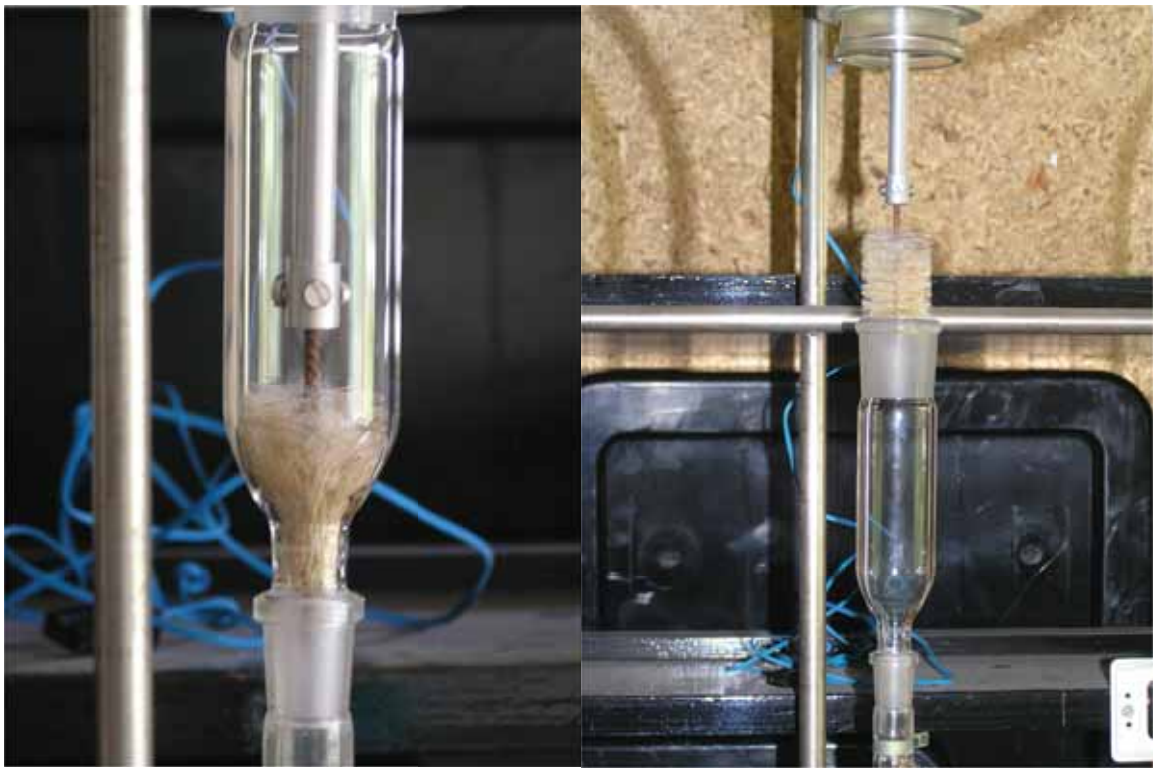

**Figure S6**. Left: Close-up of spinning brush in a simplified piptopyrolysis apparatus after assembling the device (the sample is filled on top of the brush before assemblage). Right: before assemblage. Photos by the author.

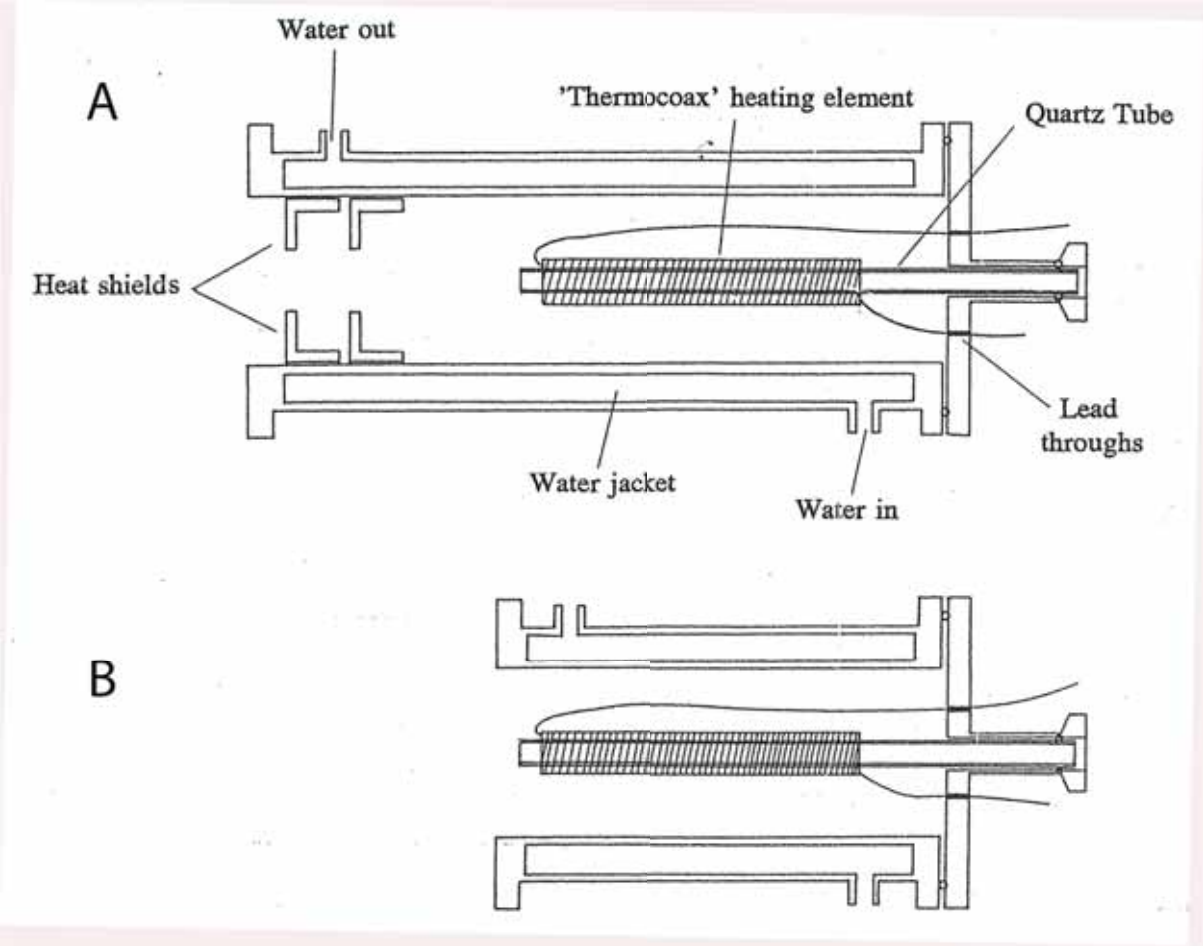


**Figure S7**. Two types of FVT ovens for use with the liq. $N_2$ or the liq. He cryostat. The sample inlet tube is flanged on the right, and the cryostat on the left. On top, two radiation shield inside the housing is seen. Design by Rodney J. Blanch and C. Wentrup

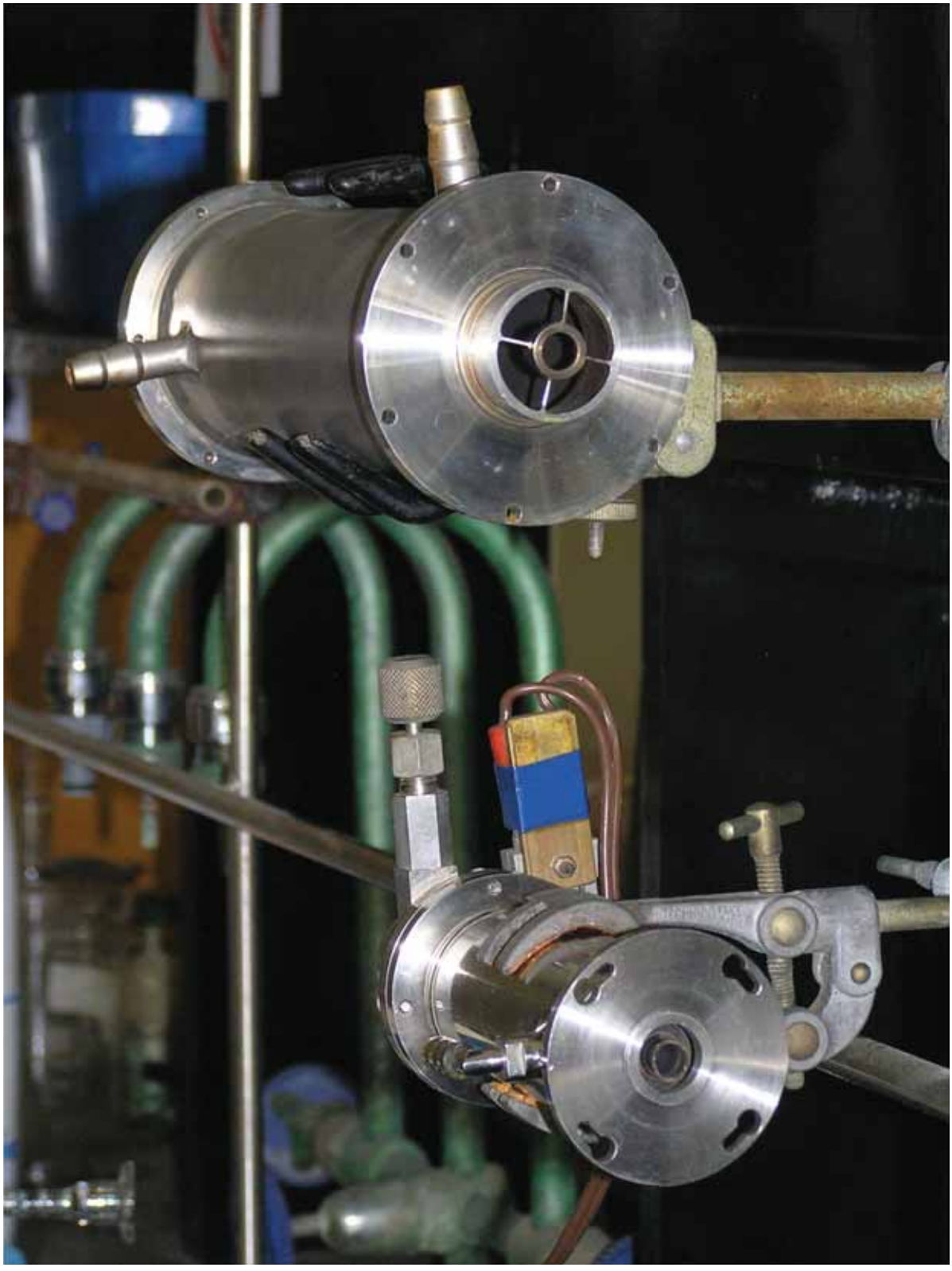

**Figure S8**. The water-cooled housings for two FVP tubes for use with the liq. $N_2$ or the liq. He cryostat. The end facing the cryostat is shown. On top, the centre ring in the cross is for holding the quartz tube in place. At the bottom, a radiation shield inside the housing is seen. The FVP tubes are in the high vacuum of the cryostat. There is no wall between the end of the tube and the cold target. For liq. He cryostat work, Ar or Xe carries the substance through the FVP tube in a ratio of ca 1000:1. Photo by the author.

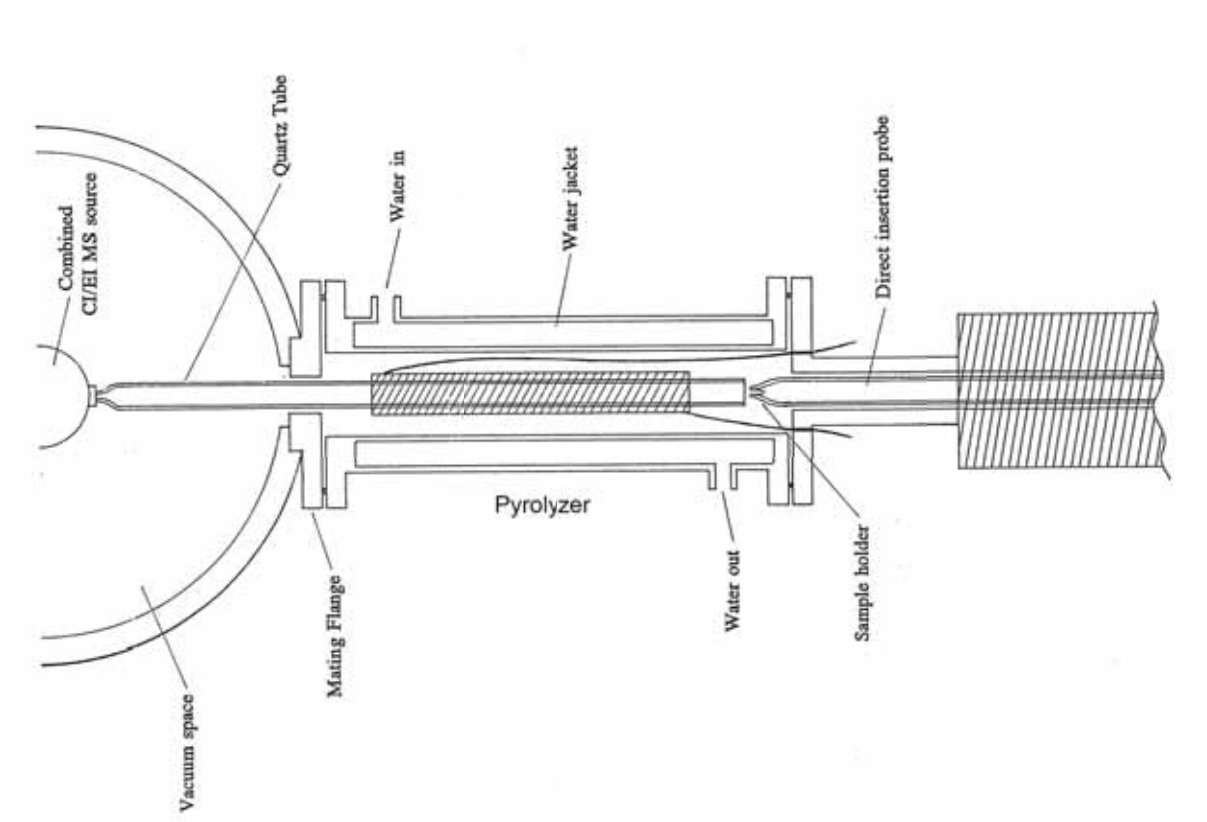


**Figure S9**. The pyrolysis unit for the Kratos MS25RFA mass spectrometer (see Figure 8 in the paper proper). Design by C. Wentrup.

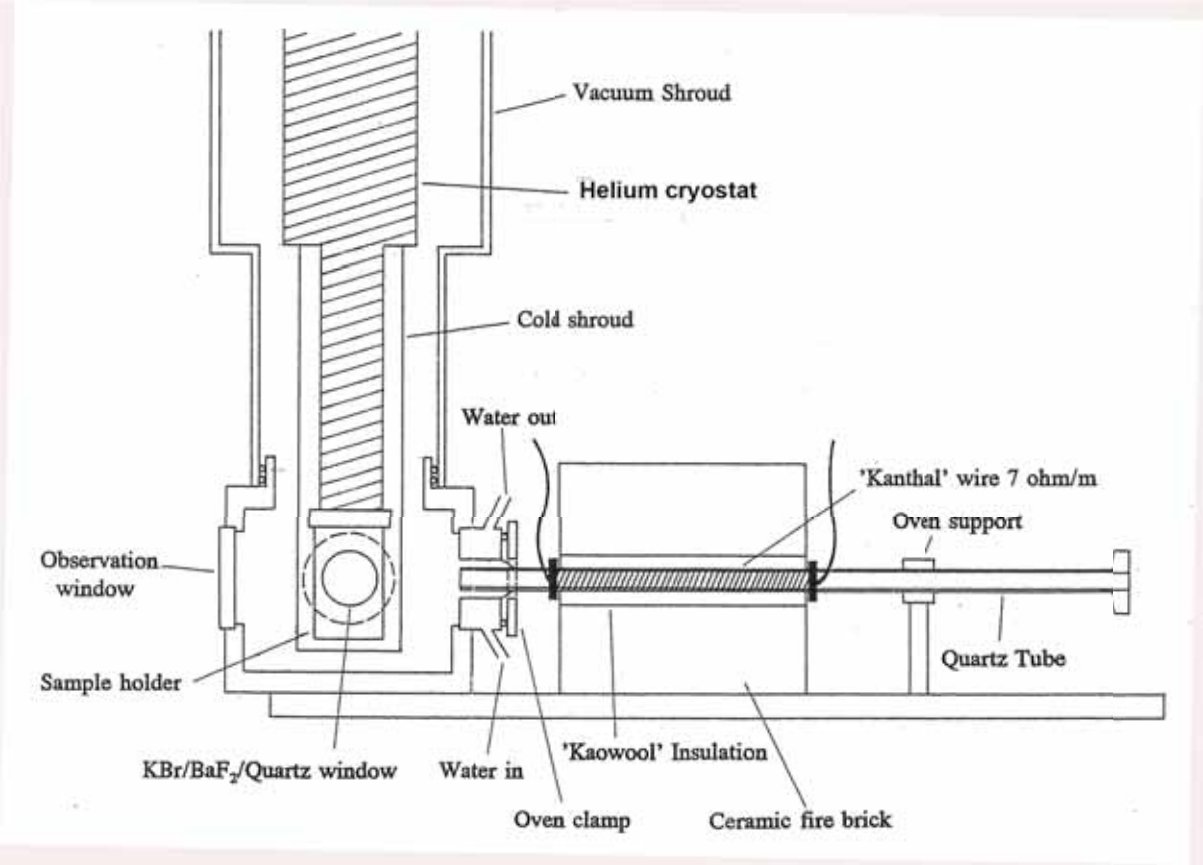


**Figure S10**. A larger scale of the schematic drawing of the "brick" pyrolyzer (Figure 10 in the paper proper). Design by Rodney J. Blanch and C. Wentrup.

**Figure S11**. Three types of "brick" pyrolyzer tubes (cf. Figure 10 in the paper proper).

A separate electric heating zone for the sample inlet is seen on the right-hand side of the upper right apparatus, where the substance is placed in a boat or a Knudsen cell. Ar or Xe gas goes through the tube from the right, entraining the substance, usually in a ratio of 1000:1.

Photo by the author

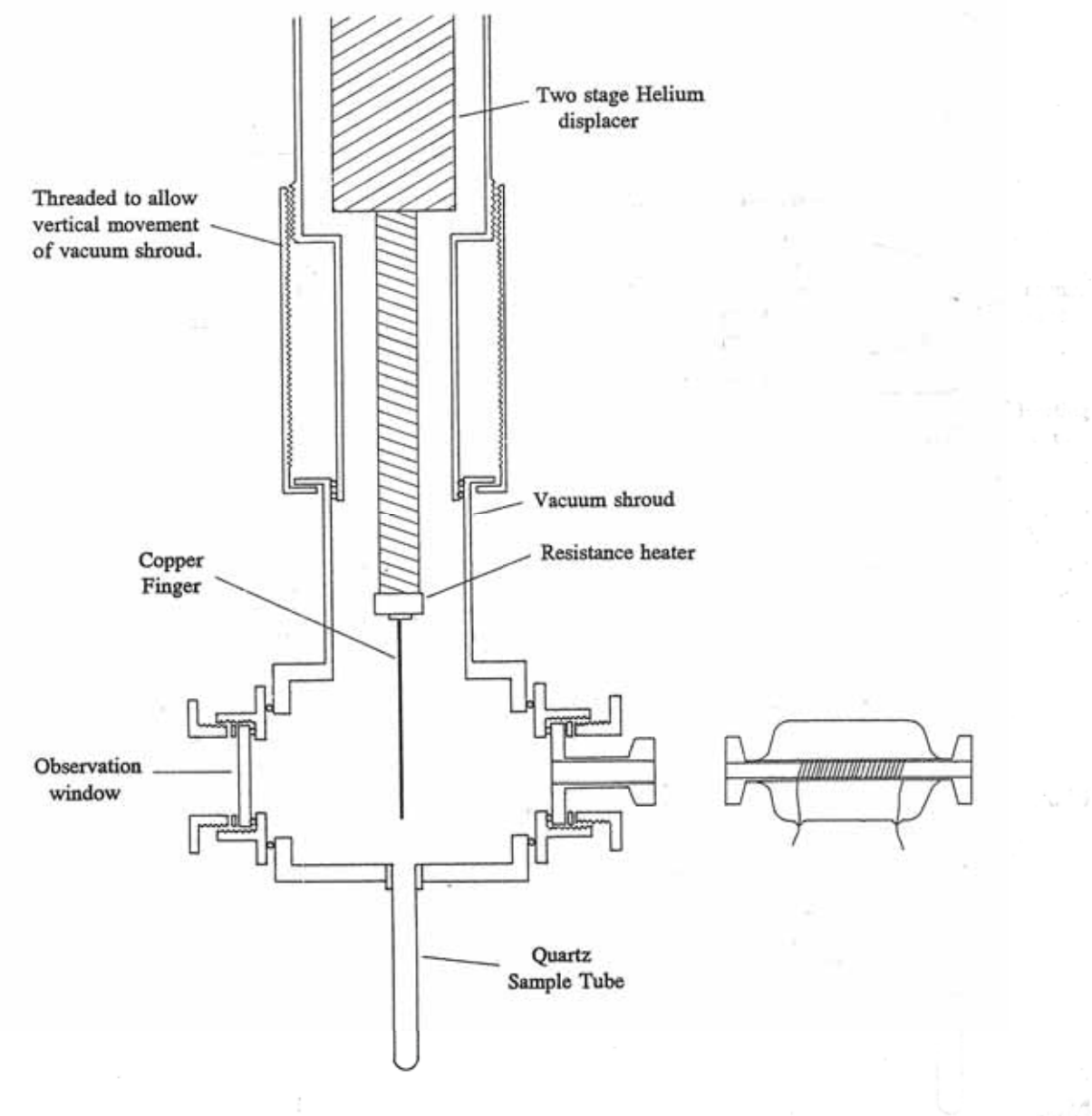


**Figure S12**. A simple sample deposition tube for use when not very high temperatures are requires, e.g. decomposition of tosylhydrazone salts to generate diazo compounds at ~100 °C, or of azides and nitrenes by FVP of tetrazoloazines at temperatures of 200-400 °C. The deposition attachment can be made of Pyrex in that case. A thermocouple and gas inlet is to be flanged to the right-hand side. The sample is placed inside the deposition tube and heated to the desired temperature; if it is very volatile, then inside a Knudsen cell, which fits into the deposition tube. The cryostat for ESR spectroscopy is shown. Design by Rodney J. Blanch and C. Wentrup