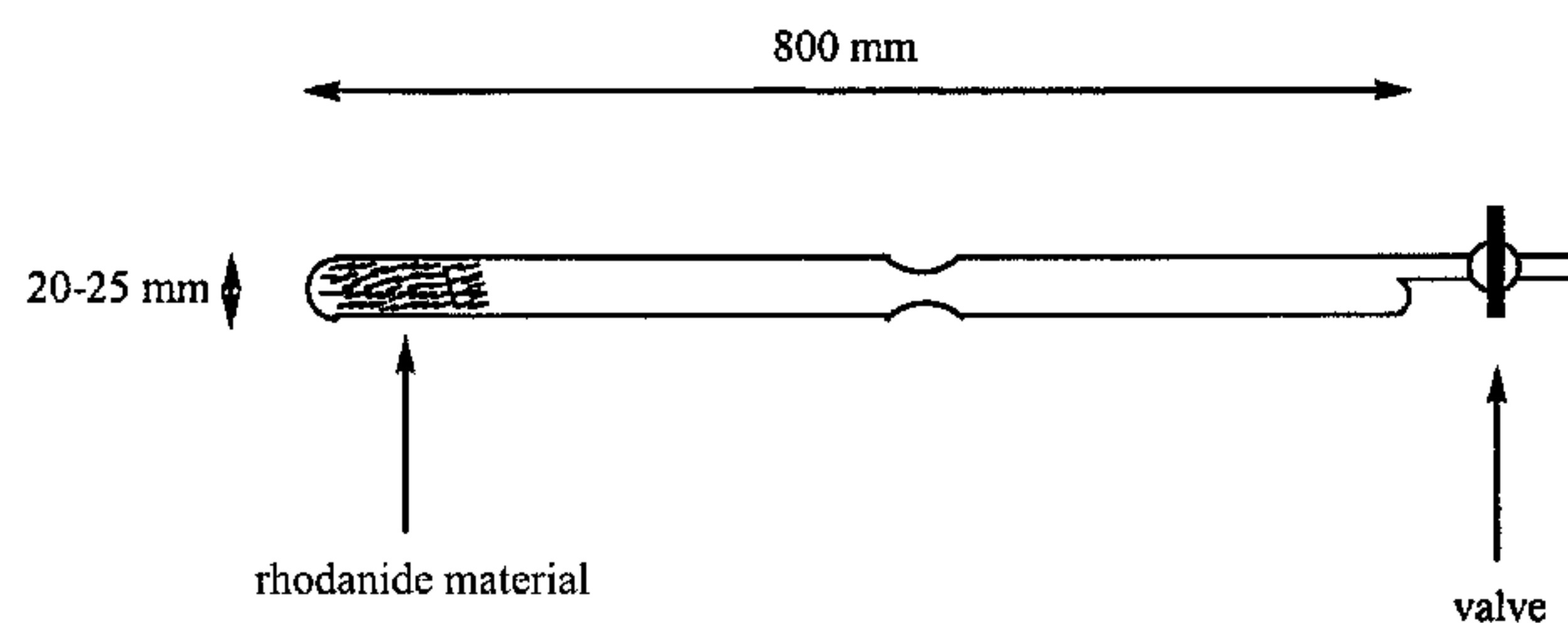




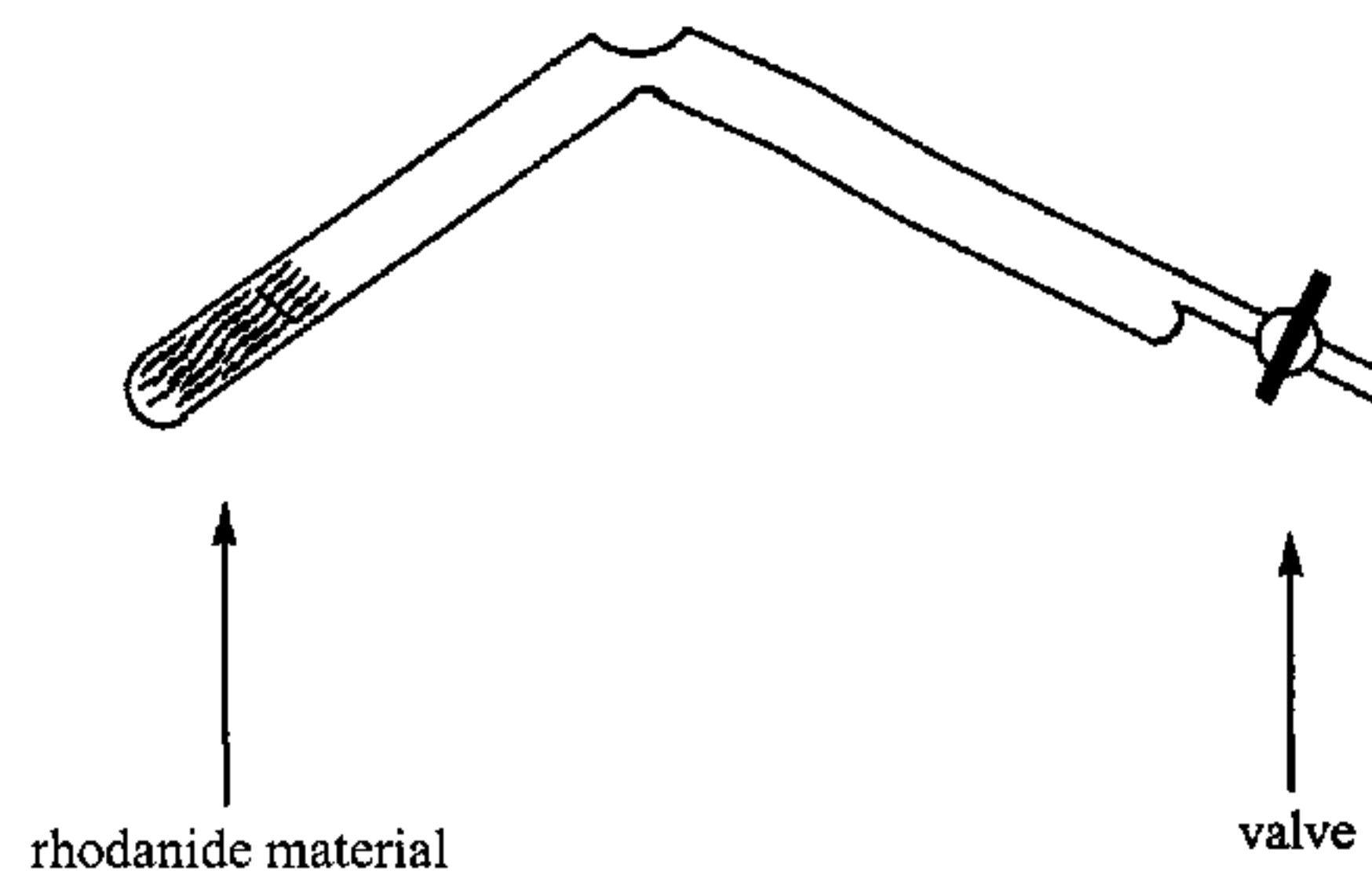
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(72) **Inventeurs/Inventors:**  
MAMAKHEL, MOHAMMAD AREF HASAN, DK;  
PHILIPPOV, SERGEJ NICOLAEVICH, RU;  
LAPPALAINEN, REIJO, FI  
(73) **Propriétaire/Owner:**  
CARBODEON LTD OY, FI  
(74) **Agent:** GOWLING LAFLEUR HENDERSON LLP

(54) **Titre : PROCEDE DE PREPARATION DE NITRURE DE CARBONE**  
(54) **Title: CARBON NITRIDE PREPARATION METHOD**



a



b

(57) **Abrégé/Abstract:**

The present invention relates to a method for preparing carbon nitride material wherein organic rhodanide is simply pyrolysed to give carbon nitride material in an efficient, economical and ecologically friendly manner. The present invention accomplishes preparation of graphitic carbon nitride materials having a carbon to nitrogen molar ratio of about 3:4. The employed starting materials are cheap and can be easily removed and/or washed away.



**Abstract**

The present invention relates to a method for preparing carbon nitride material wherein organic rhodanide is simply pyrolysed to give carbon nitride material in an efficient, economical and ecologically friendly manner. The present invention accomplishes preparation of graphitic carbon nitride materials having a carbon to nitrogen molar ratio of about 3:4. The employed starting materials are cheap and can be easily removed and/or washed away.

## Carbon nitride preparation method

### Field of the invention

This invention relates to a method for preparing graphitic carbon nitride materials having a carbon to nitrogen molar ratio of about 3:4 by pyrolysing non-metallic rhodanides in a simple and economically feasible manner. Prepared carbon nitride materials have outstanding properties and can be used in applications such as wear and corrosion resistant coatings, electronics, optical coatings and in various composite materials.

10

### State of the art

Carbon nitride materials have been the focus of considerable experimental and theoretical attention since Cohen and co-workers proposed that  $\beta$ -C<sub>3</sub>N<sub>4</sub>, a carbon nitride material analogous to  $\beta$ -Si<sub>3</sub>N<sub>4</sub>, should have hardness comparable to that of diamond. Subsequent calculations have shown that other crystalline C<sub>3</sub>N<sub>4</sub> should have stabilities comparable or greater to that of  $\beta$ -C<sub>3</sub>N<sub>4</sub>, and that many of these structures should be hard by nature. The C<sub>3</sub>N<sub>4</sub> -structures include  $\alpha$ -,  $\beta$ -, cubic-, pseudocubic-, and graphitic carbon nitride. Additionally, C<sub>2</sub>N<sub>2</sub>, although possessing different chemical structure, is called carbon nitride.

20

The local structure property that distinguishes potentially super hard and dense C<sub>3</sub>N<sub>4</sub> structures from low-density, softer material is carbon coordination: hard materials require tetrahedral or sp<sup>3</sup>-bonded carbon in the C<sub>3</sub>N<sub>4</sub> -network, while sp<sup>2</sup>-bonded carbon will lead to much softer materials. This requirement of having sp<sup>3</sup>-bonded carbon in a hard carbon nitride is completely analogous to that in amorphous diamondlike carbon (DLC), *Hu et al, Physical Review B, vol 57,1997, number 6, pages 3185-3188, Nitrogen-driven sp<sup>3</sup> to sp<sup>2</sup> transformation in carbon nitride materials.*

25

As various diamond coatings, also carbon nitride coatings possess excellent wear- and scratch-free properties. Additionally, carbon nitride materials are corrosion resistant and can act as electrical insulators, optical

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coatings, and above all, they possess remarkably better thermal resistance than obtained with corresponding DLC-coatings.

Although good results in various coating/thin film applications can already be achieved with amorphous  $CN_x$  -structures, the properties are overly enhanced once the nitrogen content and thus, the crystallinity in the carbon nitride are realized in the thin film/coating structure.

In general, the present industrially produced carbon nitride coatings/thin films are amorphous with nitrogen content less than 50%, i.e. not  $C_3N_4$  – structures.

- 10 Due to their easier availability, the amorphous  $CN_x$  –materials have already found a wide spread of applications. It is for instance the most widely used material in protective overcoats for hard disks, *Widlow et al, Brazilian Journal of Physics, 2000, vol 30, n:o 3, Recent Progress in the synthesis and characterization of amorphous and crystalline carbon nitride coatings.*
- 15 Such films are generally produced by various film deposition methods by ablating graphite in pure nitrogen the resulting films comprising amorphous carbon nitride having wear performance several times better than existing coatings.

- 20 The other efforts to produce carbon nitride coatings/thin films have been done by laser ablation, inductively coupled plasma chemical vapor deposition, solvothermal method as well as electrodeposition from organic liquid. Majority of the reports results wherein the nucleation and growth of amorphous  $CN_x$  – thin solid films takes place. In general, the materials produced in these studies have been amorphous with nitrogen content less
- 25 than 50%, i.e. not  $C_3N_4$  –structures.

- To increase the nitrogen content and the degree of crystallinity in carbon nitride films by above mentioned film deposition techniques, there have been tremendous attempts to prepare nitrogen-rich carbon nitride materials in powder form. Preferably, such precursor materials would naturally
- 30 possess carbon:nitrogen ratio of 3:4 and carbon-nitrogen bonding similar to that of  $C_3N_4$  carbon nitride materials in general.

At present, there is an actual interest in methods of production of carbon nitride by thermo chemical decomposition (pyrolysis) of chemical substances or mixtures.

There is a known method of  $C_3N_4$  production, which includes loading of  
 5 melamine  $(C_3N_3)(NH_2)_3$  and cyanuric chloride  $(C_3N_3)Cl_3$  into a reactor with further heating up and generation of the end product  $C_3N_4$ .

The drawback (of the abovementioned method) is the fact that the method does not allow to prevent the formation of  $H_2$  and  $HCN$  as by-products. This results in an elevated explosiveness and toxicity of the process; [Montigaud  
 10 H., Tanguy B., Demazeau G., Alves I., Courjault S.  $C_3N_4$ : dream or reality? Solvothermal synthesis as macroscopic samples of  $C_3N_4$  graphitic form // J. of Materials Science. 2000. V.35. pages 2547-2552].

There is also a known method of synthesis of carbon nitride  $C_3N_4$  [pat. No 6428762 US]. Powder of cyanuric chloride  $(C_3N_3)Cl_3$  is mixed with powder  
 15 of lithium nitride  $Li_3N$ , after which the mixture is placed in a reactor and sealed. Nitrogen flow is put through the reactor; the content is heated up to  $300-400^\circ C$  and incubated for a certain period of time. In order to remove any byproducts, the ready made carbon nitride is cooled down and washed.

The drawbacks of the indicated method are: the process is multistage, is of  
 20 high cost and gives a low yield of the end product -  $C_3N_4$ .

There is also a known method of  $C_3N_4$  production, taken here as a prototype. [Dale R. Miller, Jianjun Wang, Edward G. Rapid facile synthesis of nitrogen-rich carbon nitride powders // J. Mater. Chem. 2002. V. 12. P.2463-2469]. The method includes loading of trichloromelamine  
 25  $(C_3N_3)(NHCl)_3$  into a reaction chamber, after which inert conditions are ensured by a continuous flow of  $N_2$  or  $Ar$ , and in the flow of this gas environment the heating up to  $T=500^\circ C$  is carried out. There takes place a decomposition of  $(C_3N_3)(NHCl)_3 \rightarrow C_3N_{4+x} + 3HCl + (2-x)/2 N_2$  with generation of  $C_3N_{4+x}$ , where  $0.5 \leq x \leq 0.8$ . The gaseous by-products  $HCl$  and  $N_2$  are removed with the flow of the inert gas in the (reaction) chamber.  
 30 After that, the chamber is cooled down for 10 minutes, the end-product is washed with acetone and then dried at  $T=130^\circ C$ . The method does not

allow obtaining  $C_3N_4$  of stoichiometric composition; moreover, it is not possible to completely remove traces of hydrogen, chlorine and oxygen from carbon nitride.

UV photo-assisted synthesis has been employed to prepare a carbon nitride target by reacting an alkali-metal amide, such as sodium amide, as a nitrogen source with alkyl chloride, such as chloroform, as carbon source; Tien-Rong Lu, Cheng-Tzu Kuo, Teng-Ming Chen, *Thin Solid Films* 308-309 (1997), 126-129. The reaction involves steps of decomposing the unreacted starting materials by series of pumping and filtration processes, and a tedious process to remove alkali chloride by-product. The powder material is then sintered at  $800^{\circ}C$  to yield the target material containing C, N and H, the nitrogen to carbon ratio being still only 0.23.

RU2005104194 and PCT/FI2006/000040 by Lappalainen et al. describe a feasible way of producing carbon nitride ( $C_3N_4$ ) material by pyrolysing alkali metal rhodanides in a controlled manner. However, the process is limited to only alkali metal derived starting materials, non-metallic rhodanides such as ammonium rhodanide being thus excluded.

### Summary of the invention

The major drawbacks of the known methods for preparing are that they are costly, hazardous processes often comprising several reaction sequences with moderate end-product yields, with carbon:nitrogen ratios far from the desired ratio of 3:4. Moreover, the byproducts are difficult to remove and the washing processes are ineffective and time-consuming. For example when employing alkali metal rhodanides in the production of carbon nitride materials, formation of various alkali metal salts easily remaining in the carbon nitride product itself takes place. Such impurities generally have a negative effect in the product applications.

The present appropriate starting materials are very limited in scope.

The present invention now resolves the problems mentioned above.

The invention relates to a method for preparing carbon nitride materials by pyrolysing non-metallic rhodanides to give carbon nitride materials having a carbon to nitrogen ratio of about 3:4 in a simple and economically feasible manner. The method produces graphitic carbon nitride materials that can in turn be employed for preparing carbon nitride material in different chemical and structural forms including but not limited to  $\alpha$ -,  $\beta$ -, cubic-, pseudocubic-, graphitic- and amorphous forms of  $C_3N_4$ .

The carbon nitride materials have outstanding properties and can be used in applications such as wear and corrosion resistant coatings, electronics, optical coatings and in various composite materials to improve the properties of for example metal-, glass- and polymer-derived products. The carbon nitride materials can be used as additives, for example as composites in metals, metal alloys, different kinds of polymer products as well as glass products. They can be used in manufacturing of electronics and semiconductors, manufacturing of household machinery and medical equipment, drilling, grinding and polishing products, in production of blue luminophore, in spray coating of computer hard disc, manufacturing of heavy duty tools used in metal processing, as solar cell materials etc. Further, graphitic carbon nitride can be employed as fuel cell material and as a lubricant for difficult conditions. Since carbon nitride is both thermally and chemically very stable material, it will, if available in quantitative volumes, be utilized in many new applications such as coating chemical process apparatus, creep-strengthening, and improving wear and/or hardness properties of different metal grades for different purposes etc. One representative problem is for example creeping of copper materials when preserving nuclear waste for multimillennium time-frames.

Surprisingly we found that also non-metallic rhodanides such as ammonium rhodanide can be employed efficiently and in economically efficient way in preparation of carbon nitride by simply pyrolysing said rhodanides. Even when compared to pyrolysing alkali metal rhodanides, the yields are increased and the production costs are decreased further. Since no alkali metal or metal traces are formed in the reaction, the product can now be obtained without tedious washing sequences to remove said side-products.

If present, such side-products would have a seriously negative effect in the product applications.

Compared to most of the known production methods, the production cost can be lowered by factor of 10-20 via using relatively cheap raw material and raising the yield of the ready-made end product. There is provided an actual manufacturing method for quantitative production of carbon nitride materials in particle form.

As with alkali metal rhodanides, the use of organic metal rhodanide leads according to equation  $4\text{MeCNS} \rightarrow 2\text{Me}_2\text{S} + \text{C}_3\text{N}_4 + \text{CS}_2$  to generation of carbon nitride  $\text{C}_3\text{N}_4$  of stoichiometric composition and impurities, which do not contain toxic HCN, with the temperature gradient ensuring complete decomposition of the furnace charge and condensation of  $\text{CS}_2$ . Organic sulphides, which are co-produced in the reaction process, are well dissolved in water, which ensures the production of pure graphitic carbon nitride material. It was found, that by varying the temperature ramp rates and soak or annealing times of furnace charge it is possible to obtain various compositions of graphitic carbon nitride materials. As the overall size of the  $\text{C}_3\text{N}_4$  polymeric structure increases, the hydrogen content decreases and C:N –ratio approaches that of 3:4.

The pyrolysis is advantageously carried out in a reactor chamber which is built of at least two connected and sealed vessels in shape. Such features allows for making the reaction process in a closed volume, which makes the whole process ecologically-friendly, ensures the high purity and the quick removal of any by-products and reduction of the  $\text{C}_3\text{N}_4$  production costs. The process is easily up-scaleable and due to relative harmless chemicals, several different reactor materials can be employed in manufacturing apparatus. This in turn reduces the overall manufacturing cost further.

### **Brief description of the figures**

The enclosed figures represent some possible reactor vessel arrangements for preparing carbon nitride material.

**Figure 1a** represents one possible embodiment of reactor vessel arrangement for preparing carbon nitride material.

**Figure 1b** represents one possible embodiment of reactor vessel arrangement for preparing carbon nitride material.

5

### **Detailed description of the invention**

The present invention is directed to a method for preparing carbon nitride material, wherein organic rhodanide is pyrolysed to give carbon nitride material. With pyrolysis is here meant decomposition or transformation of a compound caused by heat. With rhodanides is here meant thiocyanate/iso-thiocyanate (SCN; CNS) compounds. With carbon nitride materials is hereby meant different  $CN_x$ ,  $C_2N_2$  and, especially  $C_3N_4$  materials. With organic is hereby meant all non-metallic compounds, also those not containing carbon in the molecular skeleton. With metals is hereby meant all kinds of metals, including alkali metals.

The method according to the invention enables use of all kind of non-metallic rhodanides in preparation of carbon nitride materials. An especially preferred non-metallic rhodanide is ammonium rhodanide,  $NH_4SCN$ . The rhodanides can be employed alone or as mixtures. In order to increase the production rate and/or fine tune the product structural composition, the reaction can be catalyzed with appropriate catalysts. A non-limiting example is zinc-derived catalysts, such as zinc chloride.

The pyrolysis is preferably carried out in the substantial absence of oxygen and/or hydrogen. Most preferably, the pyrolysis is carried out in complete absence of oxygen and/or hydrogen. The presence of oxygen dramatically lowers the yield of the product, and hydrogen increases the risk of explosions.

In one preferred embodiment of the invention, such conditions can be achieved by carrying out the pyrolysis in vacuumized conditions. When carrying out the pyrolysis in vacuumized conditions, the pressure can be between  $10^{-1} - 10^{-9}$  mmHg, preferably  $10^{-3} - 10^{-7}$  mmHg and most

preferably between  $10^{-4} - 10^{-6}$  mmHg, possibly using inert gas flow to remove gaseous impurities.

In another preferred embodiment of the invention, the pyrolysis of organic rhodanide or rhodanides is carried out under a high purity inert gas atmosphere. Preferably, such inert atmospheres comprise nitrogen, helium or argon.

In one preferred embodiment of the invention the pyrolysis is carried out with a gradient of  $T_{\max} \leq 850^{\circ}\text{C}$ ,  $T_{\min} \leq$  ambient temperature. In a second preferred embodiment of the invention, the pyrolysis is carried out with a gradient of  $T_{\max} \leq 650^{\circ}\text{C}$ ,  $T_{\min} \leq$  ambient temperature. In a still another preferred embodiment of the invention, the pyrolysis is carried out with a gradient of  $T_{\max} \leq 500^{\circ}\text{C}$ ,  $T_{\min} \leq$  ambient temperature. In some cases, rising the temperature over  $500^{\circ}\text{C}$  is not justifiable, as it may lead to partial decomposing of  $\text{C}_3\text{N}_4$ , thus lowering the yield of the product. Different starting materials act differently, and different temperatures can typically yield different structures of carbon nitride materials. The polymer size and thus the exact hydrogen content and C:N -ratio of the product compound can be tuned by employing different temperatures. Therefore, the scope of the invention is not restricted to said temperature gradient.

In one preferred embodiment of the invention, the temperature gradient is created essentially throughout the chamber. With chamber is here meant a reactor, in which the pyrolysis is carried out. In preferred embodiment of the invention, the formed  $\text{CS}_2$  and volatile impurities are essentially condensed in such part of the reactor, which is essentially free of carbon nitride material. Formed organic sulphide compounds such as ammonium sulphide (when employing ammonium rhodanide) can preferably be washed off the end product  $\text{C}_3\text{N}_4$  with water. The reactor is not restricted in shape or material and can be of different metal grades, glass, ceramics etc. Two possible laboratory scale quartz tube reactors are described in figures 1a and 1b.

The invention accomplishes preparation of carbon nitride material comprising graphitic structure in desired molecular ratios. Preferably, such

carbon nitride material has an atomic ratio of carbon to nitrogen of about 3:4.

Carbon nitride material is produced in particle form, but can be worked into powders, flakes, films, fibers, foams, foils, micro foils, granules, insulated  
5 wires, honey comb, dispersions, laminates, lumps, mesh, metallised films, non-woven fabrics, monofilament, rods, sheets, single crystals, spheres, tubes, wires and for example sputtering/pulsed plasma arc-discharge/laser ablation targets. Normal powder processing methods such as mixing, tabletting and sintering techniques can be utilized in production.

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### Examples

The method of the invention for preparing carbon nitride material is described below, yet without restricting the invention to the examples given here. Synthetic carbon nitride material was identified using X-ray powder  
15 diffraction, infrared absorption, and reduction melting in a carrier gas (helium) flow with subsequent chromatographic separation. The elemental analyses were conducted by employing Perkin Elmer Series II CHNS/O Analyzer 2400.

### 20 Example 1

For obtaining of carbon nitride  $C_3N_4$ , ammonium rhodanide in quantity of 10.00 g was taken, loaded into a reaction chamber, which was made of quartz glass and shaped as two connected vessels. The chamber was vacuumized to pressure of  $10^{-4} - 10^{-5}$  mmHg and sealed. The chamber was  
25 placed into an oven (Carbolite) and heated up to  $T = 600^\circ C$ , keeping the temperature gradient  $T_{max} = 600^\circ C$ ,  $T_{min} =$  ambient temperature through vessels. The following reaction was conducted for 12 hours:



Formed  $CS_2$  and volatile impurities condensed in one of the vessels due to  
30 the existence of the temperature gradient. This vessel was removed. Ammonium sulphide  $(NH_4)_2S$  dissolved readily in water, being thus readily

removed by simple washing. As a result, graphitic carbon nitride  $C_3N_4$  was obtained as a pale-brown powder, yield of which was 20%. According to the X-ray analysis, the carbon nitride material possessed carbon-nitride bonding and structure similar as reported in the state of the art. The  
 5 elemental analysis revealed the following product composition:  $C_3N_{4.5}H_{0.9}$ . No traces of sulphur or any other elements were present.

### Example 2

For obtaining of carbon nitride  $C_3N_4$ , ammonium rhodanide in quantity of  
 10 10.00 g was taken, loaded into a reaction chamber, which was made of quartz glass and shaped as two connected vessels. The chamber was vacuumized to pressure of  $10^{-3} - 10^{-4}$  mmHg and sealed. The chamber was placed into an oven (Carbolite) and heated up to  $T = 650^\circ C$ , keeping the temperature gradient  $T_{max} = 650^\circ C$ ,  $T_{min} =$  ambient temperature through  
 15 vessels. The following reaction was conducted for 12 hours:



Formed  $CS_2$  and volatile impurities condensed in one of the vessels due to the existence of the temperature gradient. This vessel was removed. Ammonium sulphide  $(NH_4)_2S$  dissolved readily in water, being thus readily  
 20 removed by simple washing. As a result, graphitic carbon nitride  $C_3N_4$  was obtained as a pale-brown powder, yield of which was 17%. According to the X-ray analysis, the carbon nitride material possessed carbon-nitride bonding and structure similar as reported in the state of the art. The elemental analysis revealed the following product composition:  $C_3N_{4.33}H_{0.87}$ .  
 25 No traces of sulphur or any other elements were present.

### Example 3

For obtaining of carbon nitride  $C_3N_4$ , ammonium rhodanide in quantity of 10.00 g was taken, loaded into a reaction chamber, which was made of  
 30 quartz glass and shaped as two connected vessels. The chamber was vacuumized to pressure of  $10^{-4} - 10^{-5}$  mmHg and sealed. The chamber was

placed into an oven (Carbolite) and heated up to  $T = 500\text{ }^{\circ}\text{C}$ , keeping the temperature gradient  $T_{\text{max}} = 500\text{ }^{\circ}\text{C}$ ,  $T_{\text{min}} = \text{ambient temperature}$  through vessels. The following reaction was conducted for 12 hours:



- 5 Formed  $\text{CS}_2$  and volatile impurities condensed in one of the vessels due to the existence of the temperature gradient. This vessel was removed. Ammonium sulphide  $(\text{NH}_4)_2\text{S}$  dissolved readily in water, being thus readily removed by simple washing. As a result, graphitic carbon nitride  $\text{C}_3\text{N}_4$  was obtained as a pale-brown powder, yield of which was 14%. According to the
- 10 X-ray analysis, the carbon nitride material possessed carbon-nitride bonding and structure similar as reported in the state of the art. The elemental analysis revealed the following product composition:  $\text{C}_3\text{N}_{4.45}\text{H}_{0.9}$ . No traces of sulphur or any other elements were present.

**What is claimed is:**

1. A method for preparing carbon nitride material, comprising pyrolysis of ammonium rhodanide to give carbon nitride material.
- 5 2. A method according to claim 1, wherein the pyrolysis is carried out under vacuum.
3. A method according to claim 1 or 2, wherein the vacuum comprises a pressure between  $10^{-1} - 10^{-9}$  mmHg.
- 10 4. A method according to claim 3, wherein the pressure is between  $10^{-3} - 10^{-7}$  mmHg.
5. A method according to claim 3, wherein the pressure is between  $10^{-4} -$   
15  $10^{-6}$  mmHg.
6. A method according to any one of claims 1 to 5, wherein the pyrolysis is carried out under an inert gas atmosphere.
- 20 7. A method according to claim 6, wherein the inert gas atmosphere comprises nitrogen.
8. A method according to claim 6, wherein the inert gas atmosphere comprises argon.
- 25 9. A method according to any one of claims 1 to 8, wherein the pyrolysis is carried out with a gradient of  $T_{\max} \leq 850$  °C,  $T_{\min} \leq$  ambient temperature.
- 30 10. A method according to any one of claims 1 to 9, wherein the pyrolysis is carried out with a gradient of  $T_{\max} \leq 650$  °C,  $T_{\min} \leq$  ambient temperature.

11. A method according to any one of claims 1 to 10, wherein the pyrolysis is carried out with a gradient of  $T_{\max} \leq 500\text{ }^{\circ}\text{C}$ ,  $T_{\min} \leq \text{ambient temperature}$ .

5 12. A method according to claim 1, wherein the carbon nitride material has a chemical formula of  $\text{C}_3\text{N}_4$ .

13. A method according to claim 1 or 12, wherein the carbon nitride material comprises graphitic structure.

10

14. A method according to any one of claims 1 to 13, wherein the carbon nitride material is produced in a manner whereby the produced carbon nitride material does not contain any traces of sulphur.

15 15. A method according to any one of claims 1 to 14, wherein the carbon nitride material is produced in a manner whereby the produced carbon nitride material does not contain any other elements than carbon, nitrogen and hydrogen.

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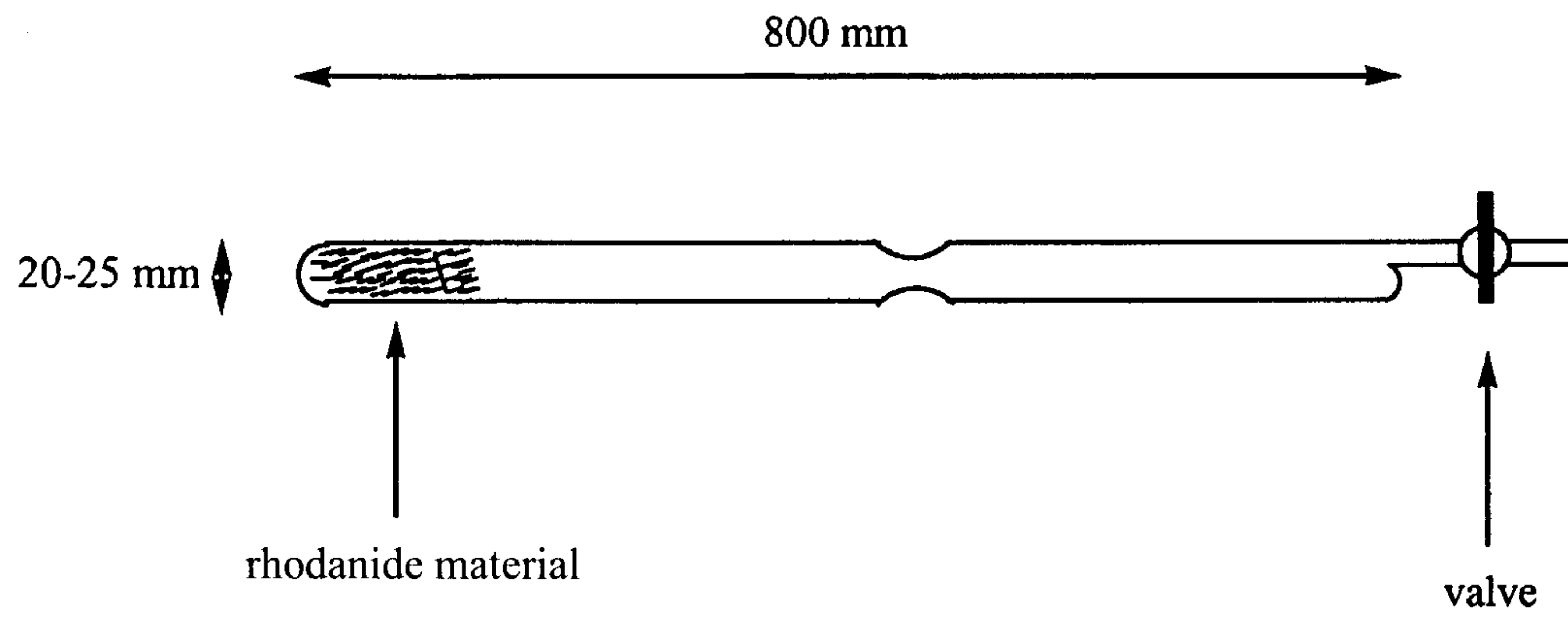


Figure 1a

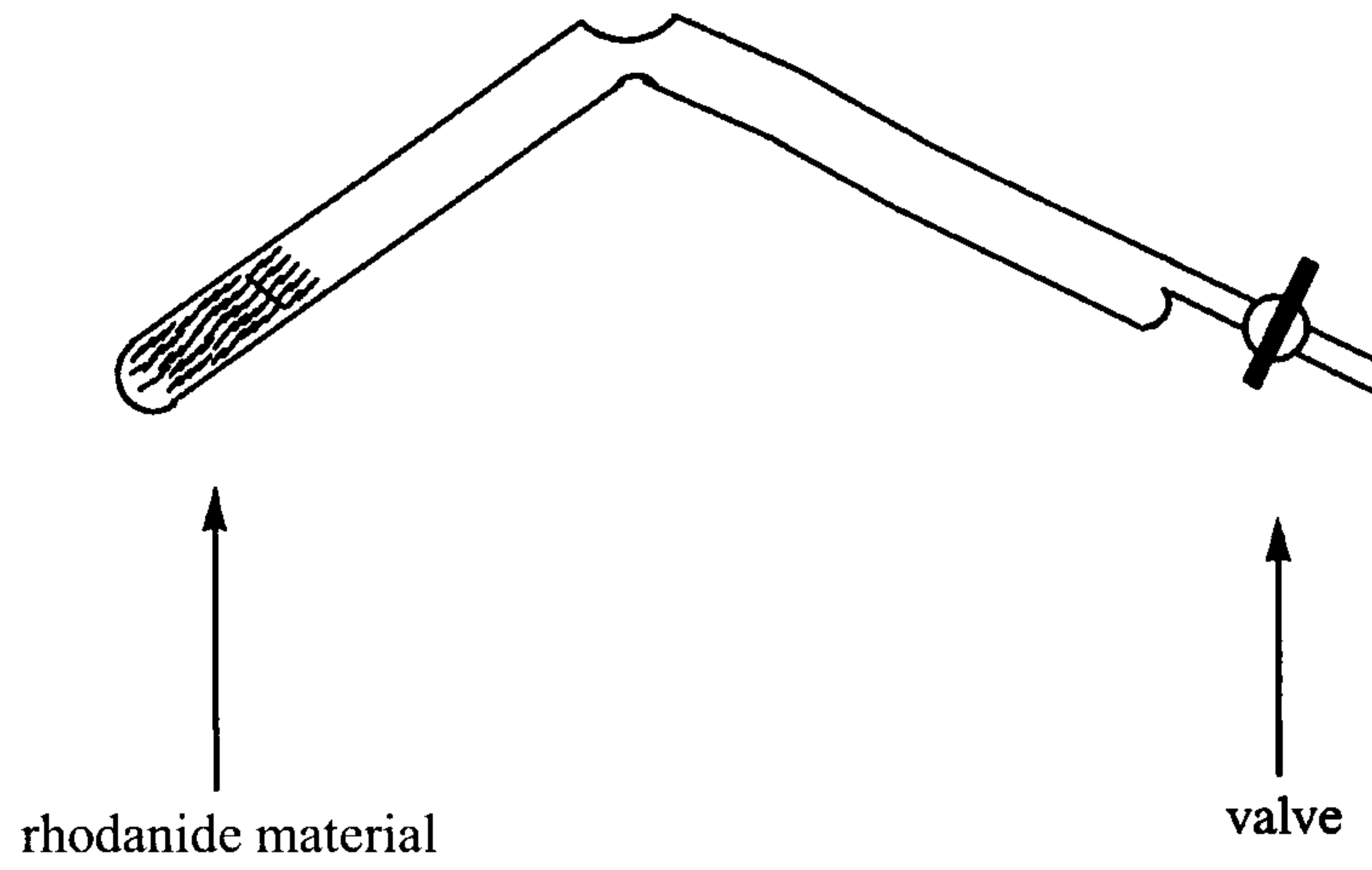
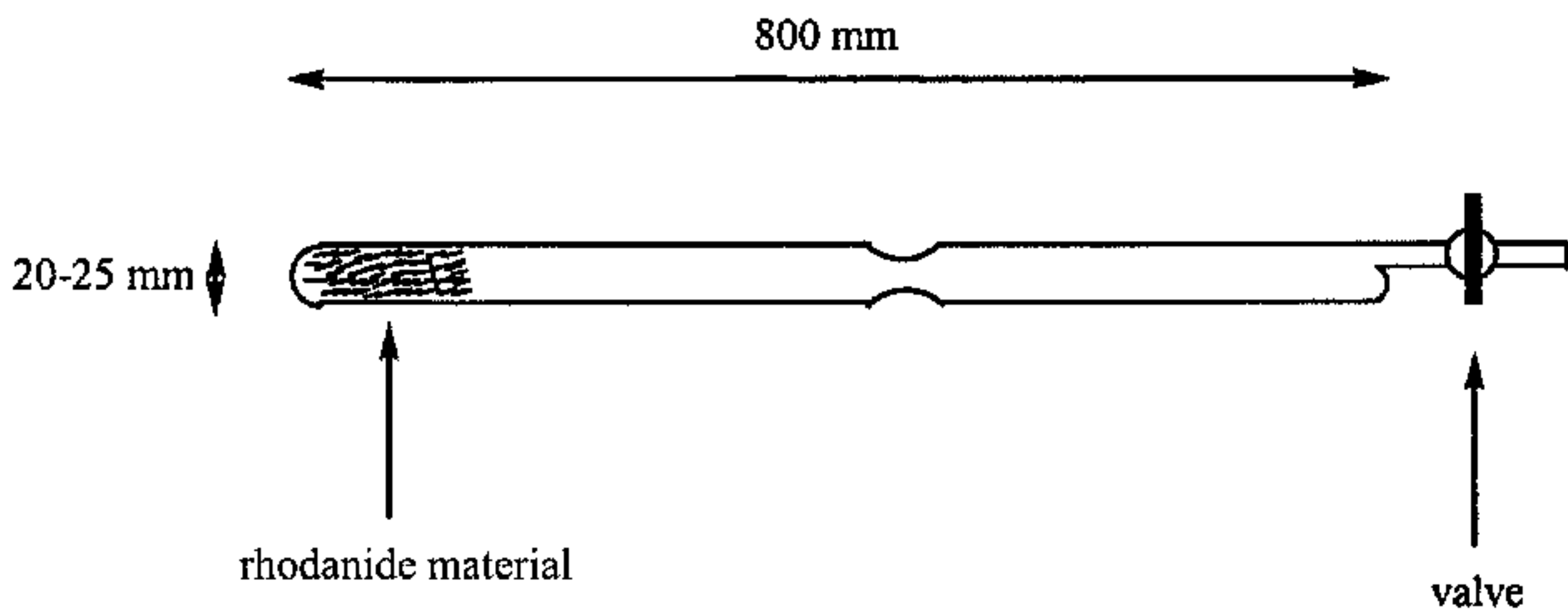
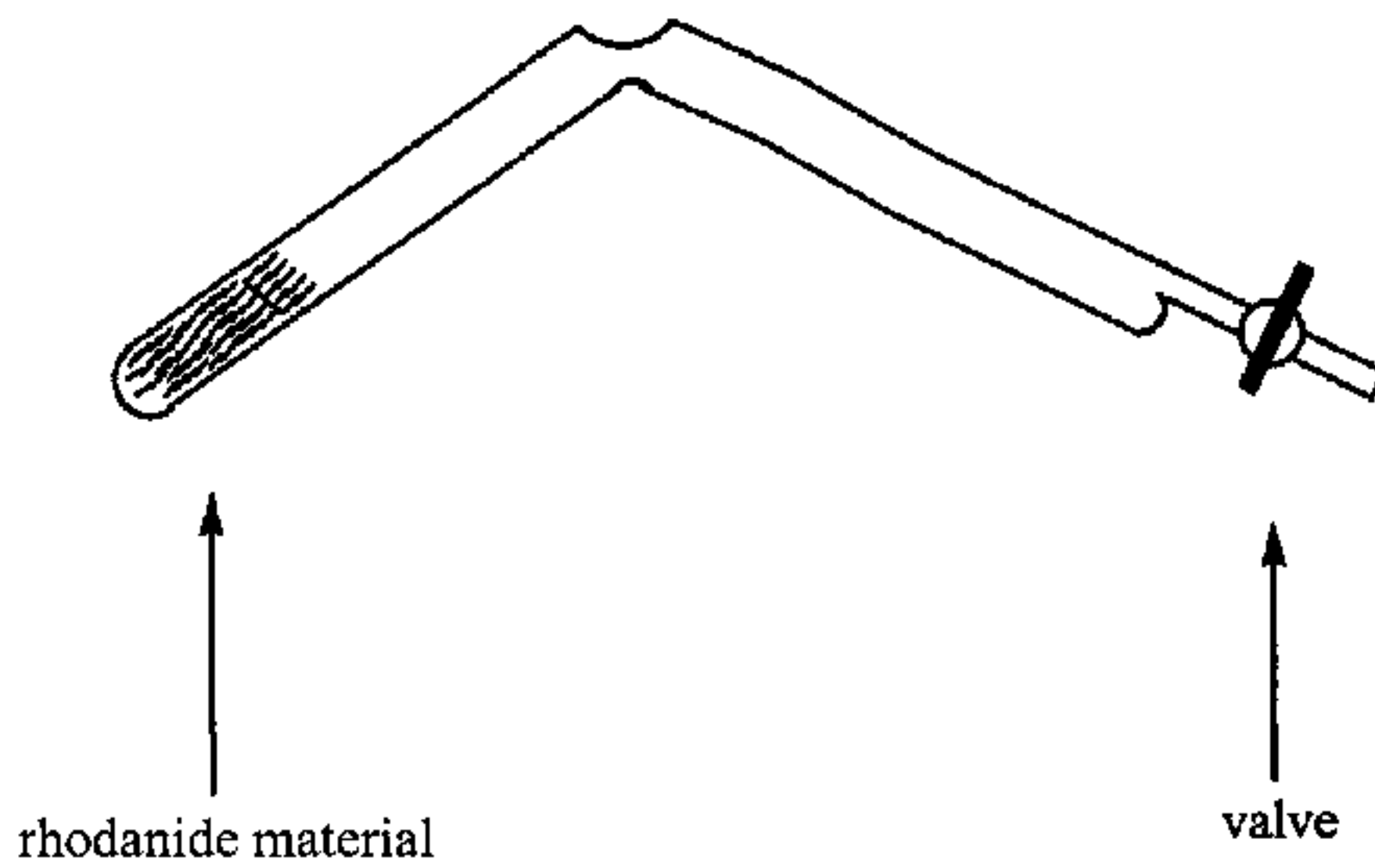


Figure 1b



a



b