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DEVELOPMENT OF A SLICING DEVICE FOR APOLLO-SOYUZ TEST PROJECT (ASTP) ELECTROPHORESIS TECHNOLOGY EXPERIMENT MA-011

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16. ABSTRACT

The electrophoresis of six columns was accomplished on the Apollo-Soyuz Test Project (ASTP). After separation, these columns were frozen in orbit and were returned for ground-based analyses. One major goal of the MA-011 experiment was the assessment of the separation achieved in orbit by slicing these frozen columns. The slicing of the frozen columns required a new device, and this report describes the development of that device.

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DEVELOPMENT OF A SLICING DEVICE FOR APOLLO-SOYUZ TEST PROJECT (ASTP) ELECTROPHORESIS TECHNOLOGY EXPERIMENT MA-011

INTRODUCTION

The Apollo-Soyuz Test Project (ASTP) presented an opportunity to perform electrophoresis in space. The MA-011 electrophoresis technology experiment was conducted to demonstrate the concept of free zonal electrophoresis in the unique environment of virtual weightlessness. Samples were processed in split glass columns as shown in Figure 1. After electrophoresis, the columns were frozen in place by the astronaut to preserve the separation attained and were returned to Earth in the frozen state. They were then sectioned by slicing, and subsequent analyses were performed on each sliced sample to further gauge the effectiveness of the electrophoretic separation. The purpose of this report is to present the engineering approach and equipment developed to accomplish this sectioning operation.

The assessment of experiment operation after flight consisted of two methods: (1) analysis of photographs taken periodically of the electrophoresis of fixed red blood cells and (2) analysis of the positions of the separated cells after return to Earth. Since photographs were not taken of the lymphocyte and kidney cell electrophoresis in space and the red blood cell photographs did not give details of the cell distribution, extraction of the cell distribution data from the frozen columns became mandatory.

The following operational limitations were important in the design of the slicing device: (1) the returned frozen sample could not at any time be subjected to a temperature above -40°C, (2) the samples could not be contaminated with external materials (e.g., particulates, solids, or microorganisms), (3) the operation was required to produce "coins" approximately 6.4 mm in diameter and from 0.5 to 5.0 mm thick, (4) the entire procedure should be recorded photographically during each cut, and (5) each slice had to be contained and stored aseptically for future examination.

Several cutting concepts were evaluated for their applicability to this task. The following types of available commercial equipment were considered: (1) microtome, (2) oscillating abrasive wire, (3) hot wire, (4) rotating wheel or

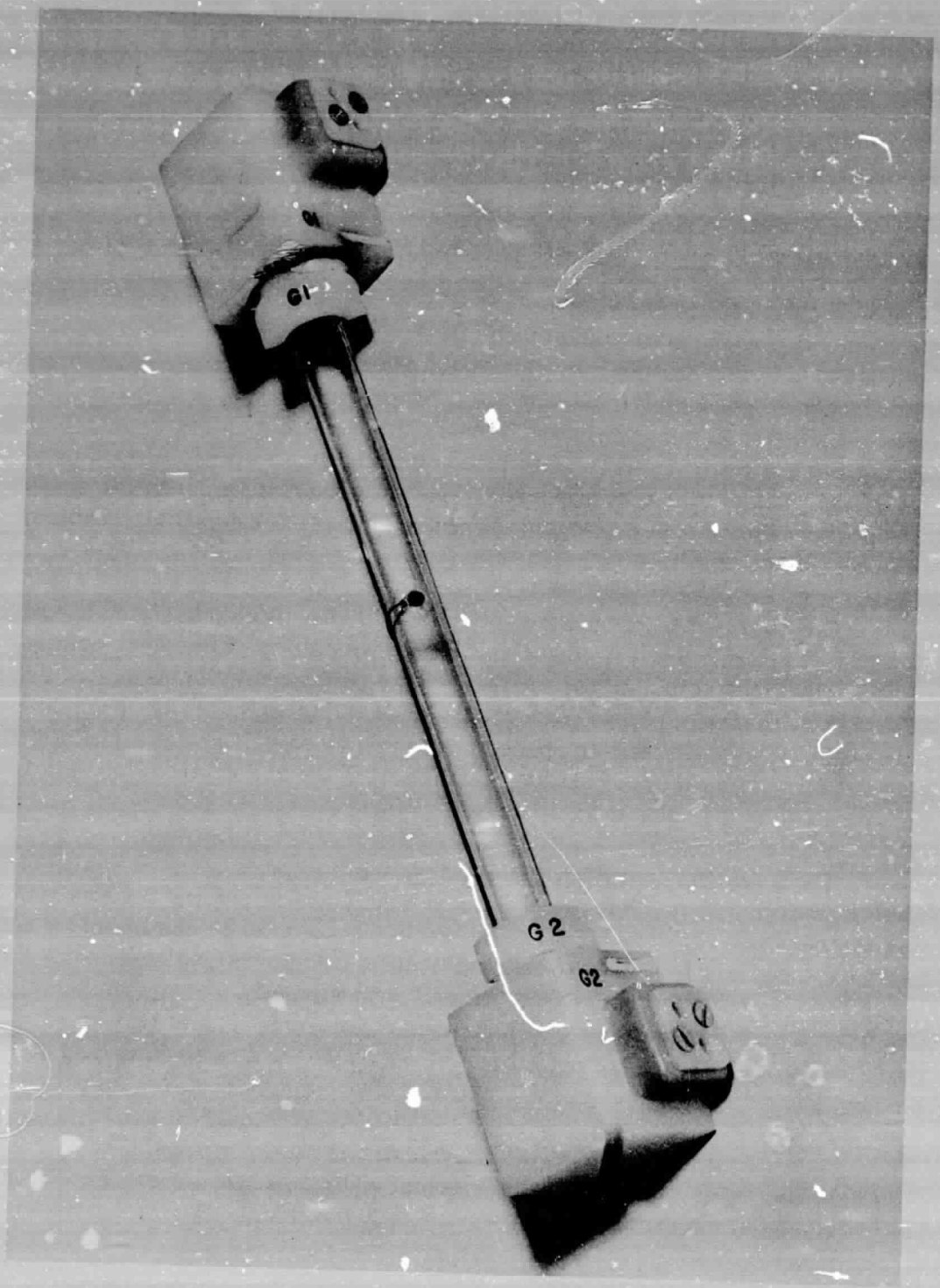

Figure 1. Electrophoresis column assembly.

blade, and (5) laser. Each commercially available system had severe limitations. For example, microtomes are designed to cut tissue imbedded in a wax block or other matrix. They could neither cut ice samples in the thickness required, nor could they keep the sample frozen during slicing. They also presented special problems when biological sterilization was considered. The oscillating abrasive wire method also had major limitations. The sample that adhered to the wire during cutting could not be recovered, and the abrasive material embedded in the wire itself tended to loosen during slicing, thus contaminating the sample. The oscillatory wire motion generated considerable heat which caused further sample loss and jeopardized the viability of the biological materials. Similar problems were encountered with the hot wire technique, which heated the viable samples and was only capable of cutting samples 5.0 mm or larger in thickness. Rotating cutting wheels or blades of diamond and carborundum were evaluated. Neither was satisfactory because they either produced excessive heat or added abrasive material to the cuts. Laser devices also appeared capable of cutting the frozen sample into large sections (4 to 5 mm), but they were unsuitable for the smaller cuts. The thermal energy was found to kill the biologicals on either side of the cut. The high cost and experimental nature of the laser equipment were also significant drawbacks.

Hence, all systems available had some major problems; however, with the information gained from the review of available hardware it was possible to design and build a cutting device which met the requirements enumerated earlier. The cutting system that evolved can best be described as a "Modified Microtome" (Fig. 2). Its operation was similar to a guillotine. The device employed a single edge stainless steel razor blade that was anchored in a special holder.

The associated equipment was as follows (see Fig. 3):

1. Blade, cutter assembly
2. Cutter assembly
3. Insulated box and cover
4. Ice remover
5. Cold plate assembly
6. Teflon tubing
7. Push rod
8. Digital distance travel indicator
9. Liquid nitrogen supply.

Figure 2. Slicing assembly.

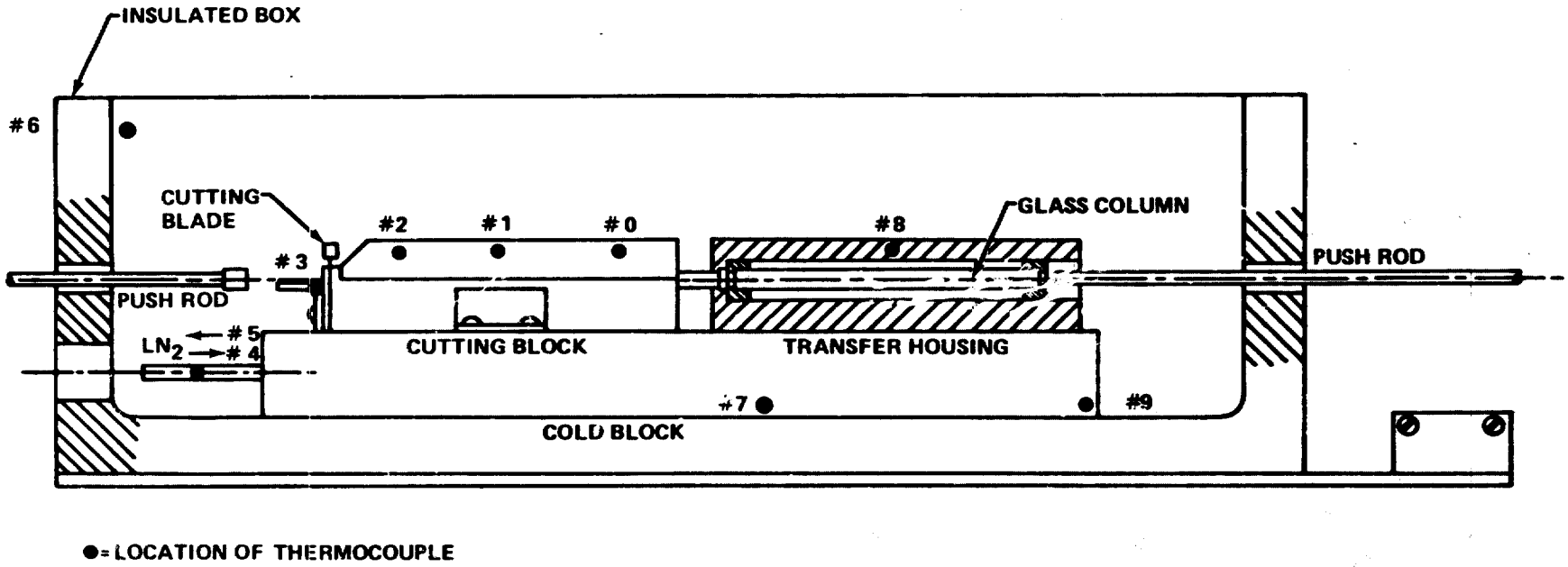

Figure 3. Cross section of slicing system.

DESCRIPTION

A. Equipment Assembly and Chilling

All slicing operations were designed to be performed within a controlled clean facility; i.e., a horizontal laminar flow bench was sterilized by wiping thoroughly with isopropyl alcohol, followed by a 1 h exposure of the area to ultraviolet radiation. The slicing hardware and associated tools were sterilized in an ethylene oxide sterilizer. Personnel involved in this operation wore clean room clothing, including a nylon coat, head cover, sterile cotton gloves under sterile surgical rubber gloves, and a surgical mask. Aseptic procedures were followed during all cutting operations.

The procedure for making the cuts involved the following steps. A cold plate was placed inside an insulated box, and liquid nitrogen (LN_2) was connected to the cooling system. The slicing fixture was then mounted on this cold plate. A 17.8 cm length of the teflon tubing, 0.635 cm inside diameter by 0.715 cm outside diameter, was inserted into the slicing fixture and installed so that it extended 1.27 cm out of the end of the fixture. The razor blade was then placed into its slot and used to trim the teflon tube to length. An extractor fixture was placed on the protruding end of the teflon which was inserted into the extractor fixture. Thermocouples were then secured in place (Table 1 and Fig. 3). A plexiglass cover was placed on the insulated box, and the flow of liquid nitrogen begun. The temperature of the fixture was reduced to between -50°C and -70°C before operations continued. Figure 4 shows the equipment in place and the temperature monitor installed.

TABLE 1. THERMOCOUPLE LOCATIONS

Channel Number	Location
0	Cutter Assembly, Right End
1	Cutter Assembly, Center
2	Cutter Assembly, Left End
3	Sample Stage
4	LN_2 Inlet
5	LN_2 Outlet
6	Flow Bench Air
7	Cooling Block
8	Sample Transfer System
9	Box Air

Figure 4. Flow bench with slicing system.

B. Column Preparation

With the slicing equipment ready for use, a frozen electrophoresis column was removed from its LN_2 storage container placed on the laminar flow bench. A "sterile wipe" was wrapped with a thermocouple around the column. The thermocouple was held in contact with the glass surface of the frozen column. A rotating diamond wheel was used to cut the plastic end fitting (Fig. 5). This operation had to be completed within 2 min to avoid melting of the frozen column.

C. Frozen Specimen Transfer and Cutting

The electrophoresis column (Fig. 5, area denoted C), was inserted into the transfer housing (Fig. 6). To avoid contaminating the frozen sample, the operator changed surgical gloves at this point in the procedure. The extraction rod was placed carefully against the exposed frozen buffer, and enough force was exerted to start the ice column moving inside the glass.

The frozen sample was advanced [illegible] it was completely transferred into the prepositioned teflon. The teflon se[illegible] to support each coin as it was cut by the blade and allowed for a smooth advance of the frozen column. The extraction device was then removed and stored in a cold sterile location.

The razor blade was then removed from the cutting slot, and the push rod was advanced slowly in the orifice of the slicing fixture (the left end) until the teflon tube and frozen section exited. This was then cut to length with a razor blade.

The driver assembly of the system was then installed as shown in Figure 7. With this driver assembly, cuts were made by advancing the threaded rod until a predetermined length of sample emerged from the slicing fixture. A "coin" of sample was then cut by a slight rocking motion of the razor blade. The cut thickness was established at 20 divisions equalling 1.0 mm.

As the samples were cut, they were placed into sterile, prechilled sample containers and stored in LN_2 freezers.

RESULTS

The slicing device operated as designed and gave the principal investigators isolated sections of frozen buffer containing the separated cells. These sections were then thawed in a prescribed manner and the cells analyzed. The

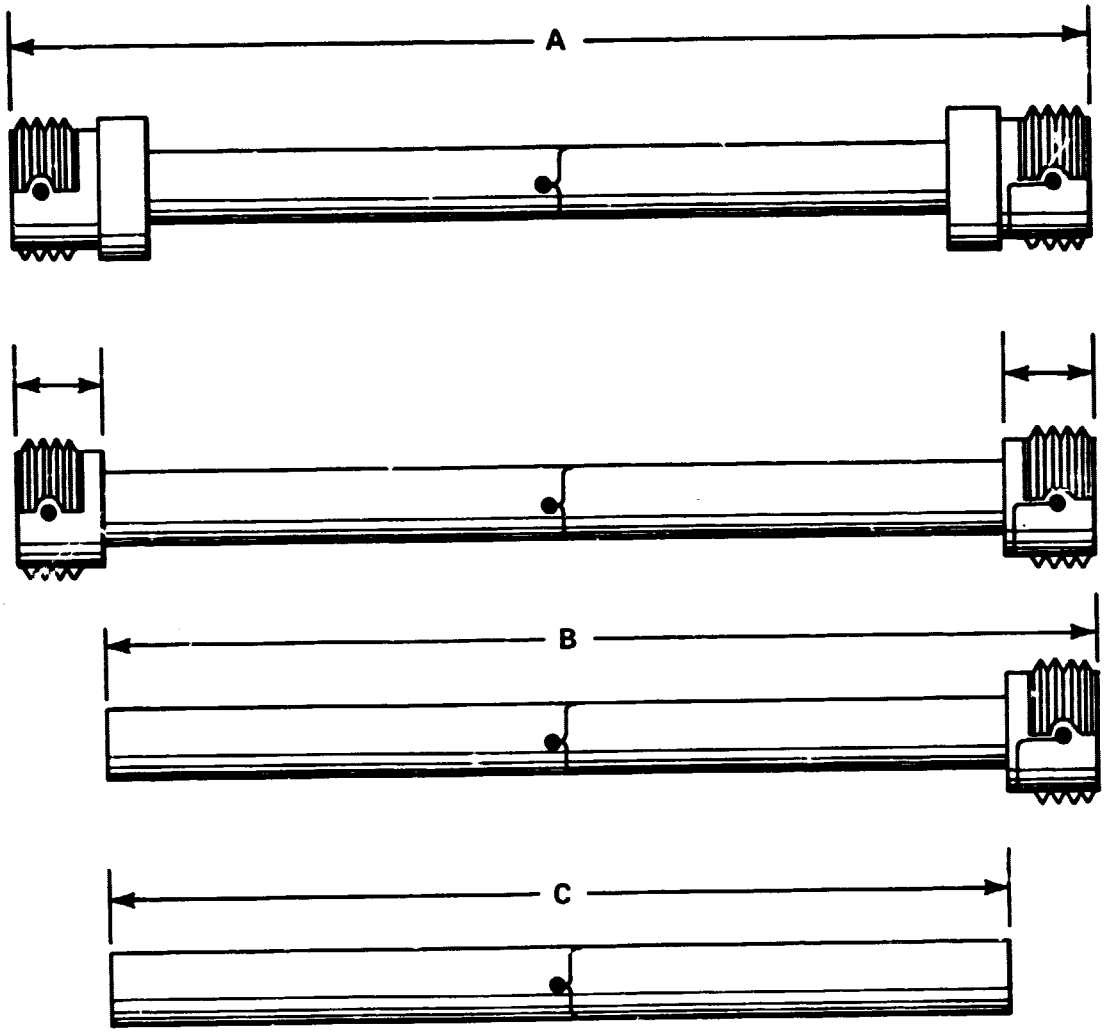

Figure 5. Electrophoresis column.

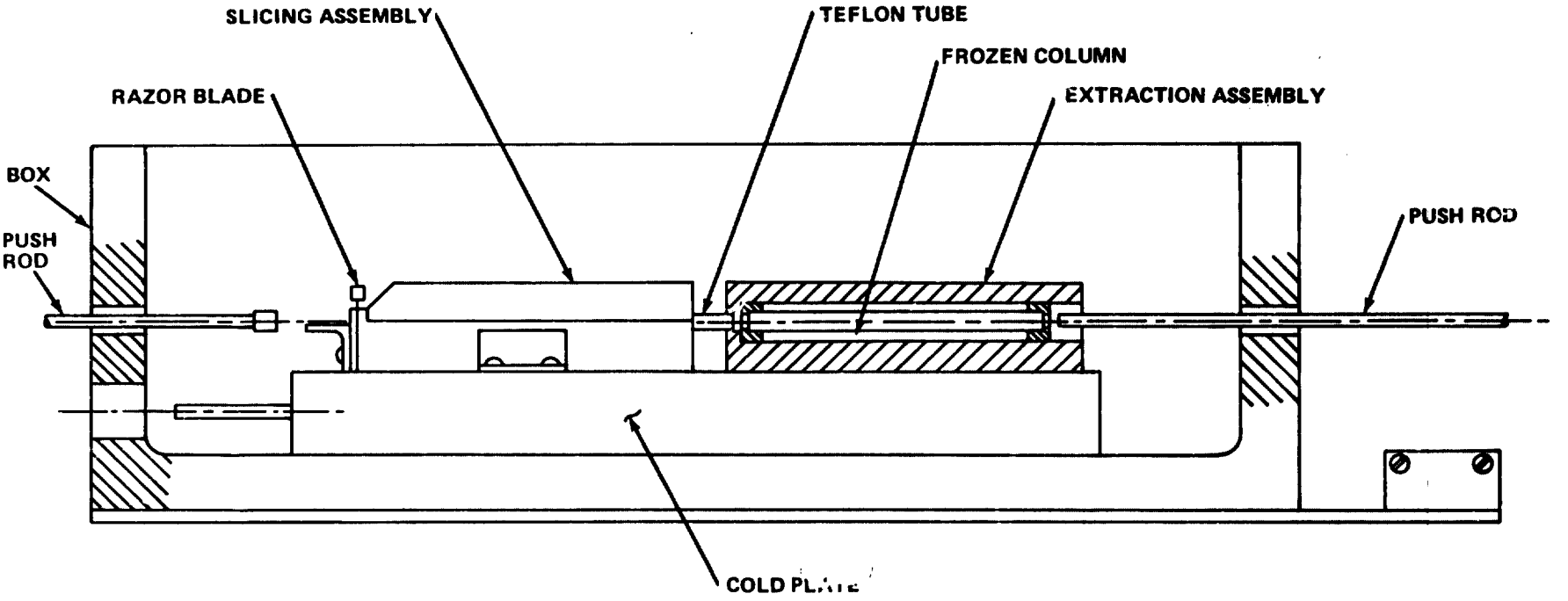

Figure 6. Cross section of slicing device showing push rods and extraction assembly.

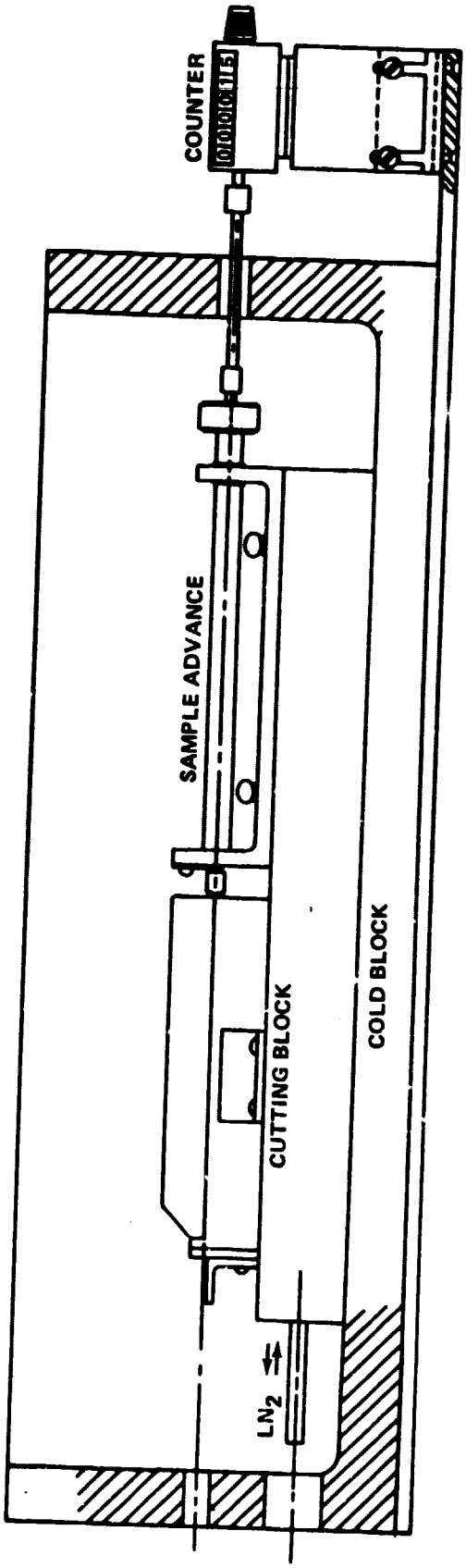

Figure 7. Cross section of slicing device showing driver assembly installed.

distribution of cell species obtained from all the isolated coins confirms the success of the ASTP Experiment MA-011, and it is anticipated that this slicing device will be used to similar advantage during experiments planned for Spacelab.

CONCLUSIONS

A survey of available off-the-shelf equipment for slicing frozen columns of water identified several techniques such as the microtome, oscillating wire, hot wire, rotating wheel, and laser. These were evaluated but were found to be inadequate. Since no device was found which incorporated the features needed in a slicing device for returned electrophoresis specimens, a microtome-like system was designed, built, and utilized to transfer and slice frozen contents of the returned electrophoresis columns. The technique developed combined features of the guillotine and the microtome, and frozen biological specimens were successfully sliced into coins 7.15 mm in diameter and 1.0 to 5.0 mm thick. This was accomplished at a low temperature without biological contamination, and evaluation of the distribution of cells in each disk provided a major source of the flight experiment results.

APPROVAL

DEVELOPMENT OF A SLICING DEVICE FOR APOLLO-SOYUZ TEST PROJECT (ASTP) ELECTROPHORESIS TECHNOLOGY EXPERIMENT MA-011

By B. H. Nerren

The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.

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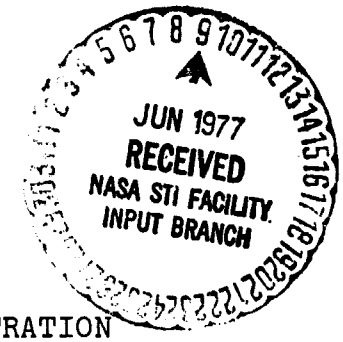
ACTIVATION OF γ-FeOOH WITH AMPHOTERIC HYDROXIDES AND ANOMALOUS BEHAVIOR OF CERTAIN COMPLEX CATALYSTS OF THIS TYPE

Alfons Krause and Jerzy Wisniewski

Translation of "O Aktywowaniu γ-FeOOH Amfoterycznymi Wodortlenkami Metali i Anormalnym Zachowaniu Sie Pewnych Katalizatorow Zlozonych Tego Typu", Roczniki Chemii, Vol. 27, 1953, pp. 232-241



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16. Abstract

γ-FeOOH is a relatively weak catalyst in the oxidation reaction of HCOOH with H_2O_2. Various amphoteric hydroxides activate γ-FeOOH. Certain complex catalysts of this type do not act according to the rules of chemical kinetics.

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ACTIVATION OF γ-FeOOH WITH AMPHOTERIC HYDROXIDES AND ANOMALOUS BEHAVIOR OF CERTAIN COMPLEX CATALYSTS OF THIS TYPE

Alfons Krause and Jerzy Wisniewski

Yellow-orange colored gel of crystalline γ-FeOOH is /232* a relatively weak catalyst in reduction-oxidation systems. It is incomparably weaker than amorphous (determined by x-ray analysis) ferric orthohydroxides. However γ-FeOOH can be activated using other amphoteric hydroxides which form with it mixed multicomponent catalysts acting efficiently in catalytic oxidation-reduction reactions. The γ-FeOOH required for the studies was obtained by us according to Krause's Polish Patent 34471 [1] by oxidation (with oxygen from the air) of ferric hydroxide precipitated from an $FeSO_4$ solution with an equivalent quantity of ammonia. Air dried γ-FeOOH contains about 17% H_2O. The activators utilized were $Cu(OH)_2$, $Mg(OH)_2$, $Pb(OH)_2$ and $Al(OH)_3$, which were precipitated using /233 an ammonia or NaOH solution (in the proper molar or atomic ratio) on moist γ-FeOOH hydrogel mixed in an aqueous salt of metal solution of the activator. After they were thoroughly washed with distilled water and dried in the air, the mixed hydroxides were used as catalysts in the oxidation reaction of formic acid with hydrogen peroxide at temperatures ranging from 20° to 50°. In addition, we used a complex catalyst, which was a mixture of air dried γ FeOOH and CuO in the proper weight ratio, pulverized jointly in an agate mortar. The CuO contained 3.1% water and similarly as all other preparations used in this study it was an analytical grade Mercowski preparation.

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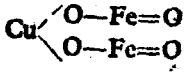
* Numbers in the margin indicate pagination in the foreign text.

Results of Studies

Among the activators mentioned, manganic and aluminum hydroxide behaved passively. $Cu(OH)_2$ precipitated on the surface of γ-FeOOH was the best catalyst with respect to γ-FeOOH. $Mg(OH)_2$ and $Pb(OH)_2$ also showed activating behavior but to a lesser degree. Both hydroxides mentioned developed fully their activating effect only after a CuO impurity was introduced into these systems. The results of these studies are presented in Tables 1 and 2 (pp. 5-6). We ascertained on one occasion that sorption of formic acid by the solid catalysts investigated (acting in a heterogeneous system) is relatively very low.

It can be seen from the tables mentioned above that the activity of the activators and the overall efficiency of complex catalysts increases considerably with increasing temperature. In particular, this applies to cupric oxide, which in the form of an impurity activates γ-FeOOH to a weak degree at a temperature of 20°, while its behavior is ideal at a temperature of 37°. Under these conditions, when its quantity is not too small (0.025 g or greater), CuO by itself is a fairly good peroxidative catalyst. Incidentally, this fact is in agreement with the results of our earlier studies [2]. The other activators mentioned above are not particularly active in an $HCOOH/H_2O_2$ system. However, above all, the fact deserving attention is that a CuO impurity can act as an activator. Probably, due to pulverizing of γ-FeOOH and CuO, closer contact is formed between the two components to a degree resulting in the formation of new active centers on the surface of the catalyst which are particularly active. This in turn suggests the assumption that mechanical pulverizing initiates not only the first stage of adsorption, but also the initial chemical reaction. Probably, incipient traces of the future chemical compound (cupric ferrite

being one of them) are already formed on this occasion. Undoubtedly, the least favorable orientation of γ-FeOOH and CuO must be assumed in this sense, the reason being that γ-FeOOH is expecially capable of forming ferrites. This is indicated by the position of its isoelectric point [3] and the ease with which silver peroxide whose formula is $AgFeO_2$ is obtained from γ-FeOOH by the wet process [4]. For these reasons γ-FeOOH has been called ferric acid [3]. Incidentally, all catalysts of this type that were investigated above should be thought of as incompletely formed ferrites which have not yet attained a definitely formed lattice structure. Probably this can be achieved under more favorable experimental conditions, for example, during calcination at an appropriate high temperature. However, in the state in which they are used as catalysts, these ferrites are in their initial formation stage. Hence they are compounds with structural defects having the character of active transient phases, which can be represented most easily schematially by writing down their radical structure



This is the fragmentary [sic] formula for the cupric ferrite radical. The radical A-Cu- activates hydrogen peroxide resulting in the formation of new radicals representing important elements of the continuous catalytic chain reaction:

the chain reaction

$$\begin{cases} A\text{—}Cu\text{—} + H_2O_2 \rightarrow A\text{—}Cu\text{—}OH + \dot{H}O \\ \dot{H}O + H_2O_2 \rightarrow H_2O + \dot{H}O_2 \\ \dot{H}O_2 + HCOOH \rightarrow H_2O + CO_2 + \dot{H}O \text{ etc.} \end{cases}$$

Since the radical 0 = Fe-0- may cause a similar reaction in which ferric and cupric peroxide compounds with a different

oxidation potential may be temporarily formed on the surface of the catalyst, the entire reaction should be interpreted on the basis of the principle of progressive multilevel catalysis in a coupled and synergetically adapted catalytic system comprising iron and copper. Under these conditions, the catalytic reaction rate increases considerably [5,6]. /236

However this does not exhaust the discussion of the system mentioned, a fact demonstrated by further detailed studies which are described in this section. The complex catalyst γ-FeOOH/CuO behaves in a much more complicated manner than an average normally working reduction-oxidation catalyst. Its activity does not follow accepted rules of chemical kinetics. The quantitative data presented in Tables 3 and 4 (pp. 9-10) /239 imply that a higher concentration of the catalyst (0.4500 g) reduces the oxidation reaction rate of formic acid compared with a smaller quantity of the catalyst (0.2250 g or 0.1125 g) which is acting more efficiently. In the case of a still smaller quantity (0.05625 g), the reaction rate decreases indeed, however, only in its initial stage (up to 200 min at a temperature of 37°), after which it increases excessively.

These examples taken from Tables 3 and 4 demonstrate that besides being complicated, the γ-FeOOH/CuO/HCOOH/H_2O_2 catalytic system is an example of a system that has not been encountered until now in the science of catalysts. The partial catalysts of this system, namely the γ-ferric hydroxide and the cupric oxide must be examined more closely and separately to explain the anomaly mentioned above. At small quantities, the activity of the latter is indeed low, however, when the CuO concentration is high, the activity of this catalyst undergoes a complete change. At this time, CuO activity is even

Table 1

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Catalytic oxidation of formic acid at a temperature of 20°

Catalyst: γ-FeOOH(0.4g) + activators as shown below. 150 ml 0.1n HCOOH + 150 ml H_2O_2 (about 0.6%). 10 ml solution = a_o ml 0.02 n NaOH.

Time min.	γ-FeOOH		γ-FeOOH +0.05gCuO		0.05 g CuO	γ-FeOOH +Cu(OH)$_2$ 1 : 1/40		γ-FeOOH +Mg(OH)$_2$ 1 : 1/5		γ-FeOOH +Mg(OH)$_2$ +CuO		γ-FeOOH +Pb(OH)$_2$ 1 : 1/24		γ-FeOOH +Pb(OH)$_2$ +CuO		Control Sample Without Catalyst HCOOH +H_2O_2
	Oxid.	Sorp.	Oxid.	Sorp.	Oxid.	Oxid.	Sorp.	Oxid.	Sor.	Oxi.	Sor.	Oxi.	Sor.	Oxi.	Sor.	
	HCOOH															
a_o →	24.8	24.8	24.7	24.8	24.8	24.8	24.8	24.8	24.8	24.8	24.9	24.7	24.8	24.8	24.7	24.8
50	24.7	·	24.5	·	24.8	24.8	·	23.6	23.8	21.9	23.6	24.4	24,7	23.6	26.6	·
100	24.6	·	24.4	·	24.5	—	·	23.5	·	20.1	·	23.9	·	22.1	·	·
200	24.6	·	23.7	·	24.2	22.0	·	23.1	·	—	·	—	·	—	·	·
300	24.4	·	22.9	·	23.8	—	·	22.8	·	14.8	·	22.0	·	11.6	·	·
400	24.3	24.7	22,0	24.6	23.3	17.8	24.6	22.5	23.7	13.6	23.5	21.0	·	7.5	·	24.8
24 hours	22.4	24,5	14.2	—	—	—	—	—	—	—	—	6.2	24.7	1.0	24.5	—

Remark: The constituents of mixed catalysts are given according to the atomic ratio of the corresponding metals. The quantity of CuO was 0.05 g in all cases.

Table 2

Catalytic Oxidation of Formic Acid at a Temperature of 37°

Catalyst: γ-Fe (0.2 g) + activators as shown below. Other details same as in Table 1

Time Min.	γ-FeOOH		γ-FeOOH +0.025g CuO		0.025g CuO	γ-FeOOH +$Mg(OH)_2$ + $Pb(OH)_2$		γ-FeOOH +$Mg(OH)_2$ + $Pb(OH)_2$+CuO		Control Sample
	Oxid.	Sorp.	Oxid.	Sorp.	Oxid.	Oxid.	Sorp.	Oxid.	Sorp.	
a,⟶	24.8	24.8	24,9	24,8	24,8	24,8	24,7	24,8	24,8	24,8
50	24.7	·	21,6	·	24,4	24,3	24,1	9,4	24,2	·
100	24.6	·	15,7	·	23,5	23,4	·	5,4	·	·
200	23.9	·	9,9	·	21,3	22,0	·	1,7	·	·
300	23,3	·	7,7	·	19,0	21,0	·	0,1	24,1	·
400	22.4	24.6	6,6	24,6	16,6	19,7	24,0	—	—	24,8

higher than that of the complex catalyst γ-FeOOH/CuO, and it is most pronounced at a temperature of 50°. This implies that γ-FeOOH exerts an inhibitory effect on the catalytic (peroxidative) properties of CuO under these conditions. Consequently, the mixed catalyst γ-FeOOH + CuO must be viewed as a system made up of two individual catalytic systems, whose action is dependent both on the first and second component of the system. The first combined catalyst comprises the basic catalyst γ-FeOOH(1), which is activated by cupric oxide. In the second case (2), Cu acts as the basic catalyst. Its activity is lowered under the effect of γ-FeOOH. It is obvious that the total efficiency of the mixed catalyst depends on the preponderance of activity (1) or (2). Hence, in this case, the catalytic reaction rate cannot be proportional to the total concentration of the catalyst.

This inefficient state of the γ-FeOOH + CuO catalyst can be corrected by introducing certain standard poisons [7]. It is well known that As_2O_3 traces undergo stronger adsorption on the surface of hydroxides. These traces are capable of cancelling considerably the inhibitory activity of γ-FeOOH. The higher As_2O_3 concentration does not cause selective poisoning, but it reduces the overall activity of the complex catalyst due to the simultaneous blocking of γ-FeOOH and CuO active centers. NaF acts similarly to As_2O_3. On the other hand, KCN behaves like a normal poison which has lost its selectivity. The poisoning activity of KCN is directly proportional to its concentration.

In view of the facts mentioned above, it appears that some caution should be exercised during an evaluation of similar mixtures of complex catalysts used sufficiently frequently in the chemical industry.

Barbara Jeske participated in the studies described above. /240

Table 3

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Catalytic Oxidation of Formic Acid at a temperature of 37°

Compound catalyst γ-FeOOH+CuO as shown below. Other details same as in Table 1.

Time Min.	0.4 g γ-FeOOH	0.4 g γ-FeOOH +0.05 g CuO	0.05 g CuO	0.2 g γ-FeOOH	0.2 g γ-FeOOH +0.025 g CuO	0.025 g CuO	0.1 g γ-FeOOH	0.1 g γ-FeOOH +0.0125 g CuO	0.125 g CuO	0.05 g γ-FeOOH	0.05 g γ-FeOOH + 0.00625 g CuO	0.00625 g CuO
0	24,8	24,8	24,8	24,8	24,8	24,8	24,8	24,9	24,8	24,8	24,8	24,8
50	24,6	21,6	23,8	24,7	21,3	24,3	24,8	22,3	24,4	24,8	23,2	24,7
100	24,3	18,4	21,6	24,5	15,7	23,4	24,8	16,8	24,1	24,7	19,6	24,3
200	23,6	15,1	16,8	24,1	9,9	21,3	24,4	7,8	22,8	24,6	11,3	23,5
300	22,9	13,2	11,9	23,5	7,7	19,0	23,8	5,1	21,7	24,2	4,9	22,6
400	21,8	11,9	7,1	22,6	6,6	17,0	23,2	3.9	20,5	23,8	2,7	21,8

Table 4

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Catalytic Oxidation of Formic Acid at a Temperature of 50°

Compound catalyst γ-FeOOH+CuO as shown below. Other details same as in Table 1.

Time Min.	0.4 g γ-FeOOH	0.4 g γ-FeOOH + 0.05 g CuO	0.05 g CuO	0.2 g γ-FeOOH	0.2 g γ-FeOOH + 0.025 g CuO	0.025 g CuO	0.1 g γ-FeOOH	0.1 g γ-FeOOH + 0.0125 g CuO	0.0125 g CuO	0.05 g γ-FeOOH	0.05 g γ-FeOOH + 0.00625 g CuO	0.00625 g CuO	Control Sample
a →	24,8	24,8	24,8	24,8	24,8	24,7	24,8	24,8	24,8	24,8	24,8	24,8	24,8
20	24,6	19,4	22,4	24,7	18,4	23,6	24,8	19,9	24,1	24,7	21,8	24,4	·
60	24,0	14,3	12,5	24,1	10,1	19,4	24,4	8,7	21,8	24,5	12,2	23,3	·
100	23,4	12,2	4,8	23,6	8,0	13,6	23,8	5,6	19,2	24,1	5,6	21,8	·
140	22,9	11,0	1,5	23,0	6,8	8,0	23,4	4,5	17,6	23,9	3,5	20,0	·
180	22,3	10,0	0,9	22,9	6,0	4,0	23,2	3,7	—	23,7	2,7	—	24,7

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