Table 1. Indexing of $NiUO_4$ and $MgUO_4$ x-ray powder patterns on an orthorhombic cell.

$MgUO_4$		*hkl*	$NiUO_4$	
d (Å)	$I : I_o$		$I : I_o$	*d* (Å)
4.67	100	110	80	4.54
3.45	10	002	15	3.41
3.28	80	200	90	3.22
2.77	80	112	100	2.73
		121,211	10	2.659
2.389	60	022	30	2.334
2.316	10	220	30	2.282
2.075	50	130,310	40	2.042
1.924	40	222	20	1.896
		123,213	10	1.789
1.782	70	132,312	70	1.754
		004	15	1.709
1.651	10	040		
1.627	40	400	30	1.605
1.560	10	141	20	1.527

from 700° to 1200°C, there was no apparent reaction; x-ray diffraction analysis disclosed only NiO and U_3O_8. These findings were consistent with the Brisi (*1*) work on uranates: by decomposing MU_3O_{10}–type compounds at 900°C, he obtained $CoUO_4$, $MnUO_4$, and $CuUO_4$, while NiU_3O_{10} decomposed to NiO and U_3O_8.

The Brisi MUO_4 compounds had the orthorhombic $MgUO_4$ crystal structure; the unit cells were larger than the $MgUO_4$ cells. Because of the smaller Ni-ion radius, the unit cell of $NiUO_4$, if it did exist, might be smaller than the $MgUO_4$ cell. It seemed possible therefore that high pressure might favor the formation of $NiUO_4$.

For the high-pressure experiment, a 1 : 1 mixture of NiO and UO_3 was fired in a sealed platinum tube, at 1100°C and 60 kb pressure, in a belt-type apparatus (*2*). The x-ray powder pattern of the resulting compound was nearly identical with that of $MgUO_4$.

The crystal structure of $MgUO_4$ was determined by Zachariasen (*3*) to be orthorhombic body-centered, with space group Iman; the powder data have not been published. In Table 1, powder data for both $NiUO_4$ and and $MgUO_4$ are indexed on the Iman orthorhombic cell. The cell dimensions for $NiUO_4$ are: a_1, 6.415 Å; a_2, 6.435 Å; and a_3, 6.835 Å. For $MgUO_4$ they are: a_1, 6.520 Å; a_2, 6.595 Å; and a_3, 6.924 Å.

Slater (*4*) has tabulated the interatomic distances in about 1000 crystalline materials; regardless of whether compounds are ionic or covalent, the observed distances between any pair of unlike atoms are generally close to the sum of the atomic radii. For the interatomic bonds to be stable, there must be some overlap between orbitals of neighboring atoms. The spacing between pairs of atoms in a crystal depends on the balance of repulsive and attractive forces between all the atoms in the crystal. If the spacing between an atom pair is close to the greatest possible distance at which orbital overlap can occur, compound formation by substitution of a slightly smaller atom for one of the pair may not be possible. However, if pressure is applied, the other bonds in the potential compound may be shortened enough to reduce the critical interatomic spacing and provide sufficient orbital overlap for crystal formation.

The Slater tabulation indicates that in the MUO_4–type compounds, $MgUO_4$ and $NiUO_4$, the M–O distances are critical in determining the stability of these compounds. In $MgUO_4$ there are two Mg–O bonds with distance 1.98 Å and four bonds with distance 2.19 Å; the latter is the greatest Mg–O distance in the Slater tabulation. Apparently, in equilibrium with the other interatomic forces, the Mg and O atoms are held apart in the $MgUO_4$ structure. If Ni and O atoms were held apart the same distance, there might not be enough orbital overlap for Ni–O bonding. The largest Ni–O spacing in the Slater tables is 2.17 Å in $NaNiO_2$. It seems likely that in crystal formation of $NiUO_4$ at high pressure the O–O and U–O bonds are shortened enough to allow sufficient overlap of Ni and O orbitals for Ni–O bonding. Once the $NiUO_4$ is formed, it is metastable at ambient pressure and room temperature. In $NiUO_4$ at ambient pressure there are two Ni–O bonds with distances 1.93 Å and four with distance 2.16 Å—close to the upper limit for Ni–O bonding.

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29 June 1966

Electrochromatography with Reversing Electrophoretic Field

Abstract. *A protein mixture can be separated in a flow column by application of a transverse electrophoretic field to carry faster-migrating components of the mixture into a fixed gel bed at one side of the column, so that slower components move along in a buffer stream. The field is then reversed to return the faster-moving components to the buffer stream. The cycle is repeated many times to complete the separation.*

We present here a process which combines the rapid migration and the resolving power of electrophoresis with the multiplier effect of a column chromatographic process to achieve improved protein separations. This technique has two unique features: (i) components are eluted in the inverse order of their electrophoretic mobilities (that is, slowest first) and (ii) a simple adjustment of electrophoretic field strength produces an effect analogous to gradient elution.

The separating column (Fig. 1) consists of a tube of rectangular cross section with a dialysis membrane and a block of gel matrix on opposing faces. We used polyacrylamide gel (*1*) to minimize endosmosis. The column was supported by Plexiglas cooling plates and was immersed in a suitable (one in which all components of interest migrate electrophoretically in the same direction) buffer solution between two electrodes which were parallel to the column. The buffer stream flowed through and completely filled the space between membrane and gel. The effluent was collected in a fraction collector or was passed directly to an analyzer cell.

The electric field from the external electrodes was passed across the column through the dialysis membrane and the gel. In one direction of the field electrophoretically faster components migrated into the gel, leaving the buffer stream enriched in slower compo-

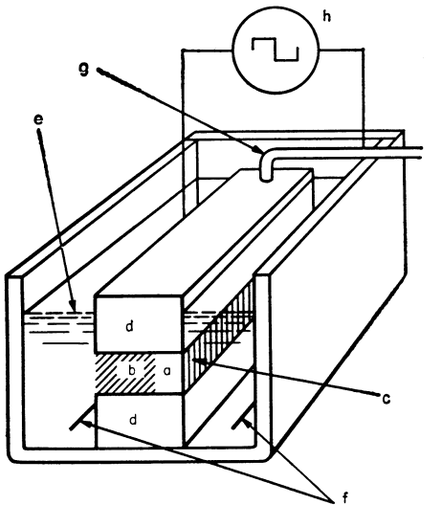

Fig. 1. Transverse alternating-current electrophoresis: *a*, separating column (1.5 by 1.5 by 240 mm); *b*, acrylamide gel reinforced with thick filter paper to give mechanical strength (1.5 by 50 by 240 mm); *c*, dialysis membrane; *d*, Plexiglas cooling plates; *e*, buffer level; *f*, electrodes; *g*, column inlet (or outlet); *h*, power supply giving a square wave output.

nents which were transported along the column by the buffer flow. In the reverse field the proteins migrated toward the dialysis membrane but they could not penetrate it. Since the forward and the reverse migrations of a protein may not be symmetrical, the timing cycle was adjusted to produce more migration toward the membrane than away from it, thus ensuring complete return of protein from the gel

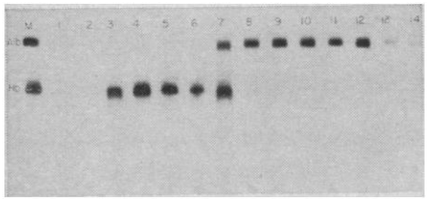

Fig. 2. A gel electropherogram showing the composition of the fractions (22 μl) from the electrophoretic column described in the text. For each cycle the column was operated at 300 volts for 85 seconds into the gel, and then for 95 seconds out of the gel. The buffer was a tris-ethylene-diaminetetraacetate-borate formulation (*4*) diluted to an ionic strength of 0.01. The gel was 7 percent Cyanogum-41 prepared in the same *p*H 8.4 buffer. The flow rate along the column was 33 μl per minute. After fraction 8, the voltage was reduced to 200 volts. Two hundred microliters of a mixture (*M*) containing 4 percent human carboxyhemoglobin (*Hb*) and a complex of 4 percent bovine serum albumin and bromphenol blue complex was initially injected into the system.

to the buffer stream. The extra migration time toward the dialysis membrane ensured complete mixing (transversely) within the buffer stream through gravitational convection and electrodecantation. Such transverse mixing is an essential step in the operating cycle (*2*). The entire cycle was repeated many times as the protein sample migrated down the column.

To begin the operation, the electric field was applied and reversed periodically, and the buffer was allowed to flow until the column reached a steady state. A small protein sample dissolved in buffer was then injected into the inlet of the column. Voltage and timing of the cycle were adjusted so that approximately one-half of the protein migrated into the gel at each reverse half-cycle, and all of it returned to the buffer stream at the forward half-cycle. In our prototype column, the sample size and the flow-rate were adjusted to permit approximately six cycles to operate before the leading protein component began to emerge from the column.

The mathematical analysis of conditions within the column, taking into account hydrodynamic flow, thermal convection, electrodecantation, and other effects, is more complex than can be conveniently presented here, but the following conclusions can be experimentally substantiated. (i) With a constant electrophoretic cycle, components emerge from the column in reverse order of their electrophoretic mobilities. (ii) By increasing the voltage, a protein of finite mobility can be retained in the column for as long as desired. (iii) Gradient elution can be achieved by initiating operation with a higher voltage and then reducing voltage gradually to elute components with higher mobilities (in sequence).

For a preliminary demonstration of these principles, a mixture of human hemoglobin and a complex of serum albumin and bromphenol blue was used so that the process could be followed visually (Fig. 2). The recovered fractions were analyzed by conventional gel electrophoresis (*1*). Despite the large sample volume employed (in comparison to channel volume), which limited the number of times the field reversal could be applied, the two components were completely separated.

This apparatus also offers interesting possibilities in the study of electrophoretic processes. Extremely high fields can be applied for very short periods, without exceeding the average power input capacity of the column, making it possible to study potential effects of high voltages in electrophoretic transport (*3*).

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Chemical Pruning of Plants

Abstract. *The lower alkyl esters of the C_8 to C_{12} fatty acids and the C_8 to C_{10} fatty alcohols selectively kill or inhibit the terminal meristem without damaging the axillary meristems, foliage, or stem tissue of a wide variety of plants. The axillary meristems develop at nearly the same time as those of plants whose terminal meristems have been removed manually. The concentration of the fatty acid esters and alcohols required to kill the terminal meristem range from 0.025 to 0.05*M *for herbaceous plants, 0.05 to 0.16*M *for semi-woody plants, and 0.16 to 0.27*M *for woody plants.*

Tso (*1*) reported that the alkyl esters of the C_9 to C_{12} fatty acids inhibited the growth of axillary buds when applied to tobacco plants whose tops had been removed. Only the meristematic cells of the buds were destroyed by the chemical. The leaves of the treated plants were unaffected. The methyl ester was found by Tso, Steffens, and Engelhaupt (*2*) to be more effective than the isopropyl and butyl esters.

We report that lower alkyl esters of the C_8 to C_{12} fatty acids and the C_8 to C_{10} fatty alcohols in aqueous emulsions selectively killed the terminal meristems of a wide variety of plants without damaging the axillary meristems, foliage, or stem tissues of the plants. The plants were sprayed with the minimum amount of emulsion to wet all surfaces. The first visible