other into a beaker in which the tube is immersed. The resistance of shale specimens so mounted varies, but the total resistance is of the order of 10,000–20,000 ohms, and satisfactory potential readings can be made with a Leeds & Northrup Type K potentiometer. A thermionic amplifier is not necessary unless the total resistance exceeds 20,000 ohms. Saturated calomel electrodes were employed as measuring electrodes, the usual precautions being taken to ensure reproducible boundary potentials between the saline solutions and the saturated potassium chloride bridges.

Results obtained using the shales to separate sodium chloride solutions of various molalities were very consistent provided the shales used were uncracked. Where appreciable cracking was present but unnoticed prior to mounting the specimens, erratic potentials were immediately observed, and the cracks themselves soon became visible, the shales frequently shearing at the point of cracking. Attainment of equilibrium after changing the saline solutions was usually rapid unless a big change in the concentration of the solutions had been made, in which case equilibrium was only achieved after a period of days with frequent changing of the sodium chloride solutions.

TABLE 1

Shale type	a_1	a_2	Calculated potential (mv)	Observed potential (mv)
Conemaugh Woodford	0.0398	0.0101	32.7	32.7
Conemaugh Woodford	0.395	0.0995	32.2	32.2
Conemaugh Woodford	0.719	0.2856	23.3	23.0

TABLE 2

Shale type	C_1 molal	C_2 molal	Potential from conductivity	Observed potential (mv)
Conemaugh	2.0	0.5	30.1	14.3
"	4.0	1.0	23.7	9.9
Woodford	2.0	0.5	30.1	34.2
"	4.0	1.0	23.7	28.9
"	Saturated	0.01	133.5	137.2

In Tables 1 and 2, calculated potentials up to 1.0 molal have been derived from activities in the manner discussed above. For concentrations between 1.0 molal and saturation each ratio of the sodium ion activities in the Nernst equation has been replaced by the comparable ratio of the conductivities of the two sodium chloride solutions. This has been done because the computation of sodium ion activities at very high concentrations involves large uncertainties. The conductivity data used are not of the highest accuracy, but comparison of potentials calculated from the conductivities with observed values serve to show that the analogous shale potentials recorded in the electrical well logging of deep boreholes may be used to obtain an estimate of the conductivity of the saline fluids in petroleum reservoir rocks (*7*). Results are for a temperature of 20° C.

The data show that both the Conemaugh and Woodford shales appear to have marked sodium electrode properties at concentrations up to 1.0 molal, but beyond this concentration the ability of the Conemaugh to give potentials of the magnitude required by the Nernst equation is markedly inferior to that of the Woodford. This difference in behavior probably results from the varying nature of the minerals and interstitial waters in the two shales. In the case of Conemaugh shales there were no electrochemical differences between the red and gray facies examined, indicating that the state of reduction of the iron in the shales is not a primary factor.

No theory to cover the behavior of the Woodford shale is at present available, but the results show that it may be possible to produce a membrane from shales which will encompass an activity range, for sodium ions, considerably wider than that covered by any of Marshall's prepared clay electrodes. Assuming that it is justifiable to extend the application of the Meyer and Sievers and Teorell theories to cover the very high sodium chloride concentrations used in these experiments, it would appear that the thermodynamic charge, A, on the shale minerals —possibly the clay minerals in the shales—is relatively very large. Work on shale membranes is continuing.

References

1. LATIMER, W. M. *Oxidation potentials.* New York: Prentice-Hall, 1938.
2. MARSHALL, C. E. *J. phys. Chem.*, 1939, **43**, 1155; 1944, **48**, 67.
3. MARSHALL, C. E., and BERGMAN, W. E. *J. Amer. chem. Soc.*, 1941, **63**, 1911; *J. phys. Chem.*, 1942, **46**, 52, 325.
4. MARSHALL, C. E., and KRINBILL, C. A. *J. Amer. chem. Soc.*, 1942, **64**, 1814.
5. MEYER, K. H., and SIEVERS, J. F. *Helv. Chim. Acta*, 1936, **19**, 649, 665, 987.
6. TEORELL, T. *Proc. Soc. exp. Biol. Med.*, 1935, **33**, 282; *Trans. Faraday Soc.*, 1937, **33**, 1054.
7. WYLLIE, M. R. J. A Quantitative Analysis of the Electrochemical Component of the S.P. Curve. AIME Preprint, October 1948. (To be published in *Petroleum Technology*, January 1949.)

Carbon Dioxide, Cerebellum, Chloramines, and Convulsions

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During the past two years much light has been shed on the problem of the convulsant agent in bleached flour. Since the observation of Mellanby in December 1946 (*4*), that treatment of flour with nitrogen trichloride as used commercially makes such flour toxic to dogs, there has been much speculation regarding the possible effect of such a diet on man. Human experimentation is being carried on in at least three institutions, and it is too early to evaluate results obtained thus far.

We are reporting here certain observations made upon dogs fed diets containing agenized (NCl_3-treated) proteins. These observations may help to identify the toxic compound or compounds and to determine human susceptibility.

Nitrogen trichloride (NCl_3) may be prepared by the interaction of chlorine gas and ammonium chloride solution. If the pH of the reaction mixture is raised above 4.5, increasing amounts of homologues of NCl_3 are formed, namely, $NHCl_2$ (dichloramine) and NH_2Cl (monochloramine) (*1*). It is of considerable theoretical interest that these latter chloramines *do not* produce in flour a detectable convulsant compound. Only trichloramine (NCl_3) is capable of reacting with protein to produce a convulsant agent which is active after oral administration.

A similar reaction product, identified by its physiologic and electroencephalographic effects, can be produced in the wheat proteins gliadin and glutenin, the corn protein zein, and the milk proteins casein and lactalbumin (*5, 8*). When similar amounts of these proteins have reacted with equal amounts of gaseous NCl_3, the resultant toxicity appears to be proportional to the sulfur content of the original protein and not to be correlated with any other portion of the amino acid composition of said proteins (*6*). If these agenized proteins are hydrolyzed by tryptic digestion, the soluble amino acid residues retain about 50% of the convulsive toxicity of the whole protein, and they appear to be more potent by the oral than by the intravenous route. A number of laboratories are now engaged in the attempted isolation of the altered amino acid or polypeptide responsible for the convulsions.

The effects of this unknown compound are as yet best analyzed by means of the electroencephalogram. An altered EEG appears before the overt convulsion, and the seizure pattern as seen with the EEG is characteristic and significantly different from that produced by other convulsants, e.g. Metrazol or strychnine (*7*). These characteristics form the basis for this communication. First, a seizure may be provoked in a susceptible animal (dog on a bleached diet for 3 days) by the inhalation of a mixture of 20% carbon dioxide and 80% oxygen. This is somewhat surprising in view of the known "depressant" effect of CO_2 on the cerebral and cerebellar cortex. Secondly, the seizure as recorded by the electroencephalogram, whether occurring spontaneously or provoked by CO_2 inhalation, is seen to arise in the cerebellum (or at least is recorded from cerebellar leads) a few seconds before the seizure is seen in the cerebral cortex. That the cerebellum has the capacity to convulse has been appreciated although little emphasized, but that it has the capacity to "drive" the cerebral cortex into a typical tonic-clonic seizure, or that both cerebrum and cerebellum are driven almost simultaneously from a subcortical locus, would tend to establish agene convulsions (along with DDT convulsions) as a unique entity in the much explored fields of human and experimental epilepsy.

If the reaction product between NCl_3 and the protein moiety can be identified, we shall be much closer to an understanding of how it can induce convulsions. Until that time we must speculate regarding the mechanism by which certain low-molecular-weight chlorinated compounds (e.g. DDT) can produce electrical changes in the cerebellum along with cerebellar degeneration (*2, 3*), and as to why the reaction of proteins with certain chloramines and not with others can produce seizures and degeneration in the cerebellum while making the cerebral cortex more susceptible to activation by CO_2. This may well be a case where intensive investigation of what is at first sight a purely nutritional problem will yield fruitful results in the analysis of fundamental neurophysiological mechanisms.

References

1. Chapin, R. W. *J. Amer. chem. Soc.*, 1929, **51**, 2112–2117.
2. Crescittelli, F., and Gilman, A. *Amer. J. Physiol.*, 1946, **147**, 127–137.
3. Haymaker, W., Ginzler, A. M., and Ferguson, R. L. *Amer. J. med. Sci.*, 1946, **212**, 423–431.
4. Mellanby, E. *Brit. med. J.*, 1946, **2**, 885–887.
5. Moran, T. *Lancet*, 1947, **2**, 289–291.
6. Silver, M. L., Johnson, R. E., Kark, R. M., Klein, J. R., Monahan, E. P., and Zevin, S. S. *J.A.M.A.*, 1947, **135**, 757–760.
7. Silver, M. L., Monahan, E. P., Klein, J. R., and Pollock, G. H. *Arch. Neurol. Psychiat.*, in press.
8. Silver, M. L., Zevin, S. S., Kark, R. M., and Johnson, R. E. *Proc. Soc. exp. Biol. Med.*, 1947, **66**, 408–409.

Construction of Glass Diaphragm Leaks for Gas Analysis With a Mass Spectrometer

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It has been shown (*1*) that the requirements of gas flow necessary to perform satisfactory gas analyses with a mass spectrometer are fulfilled essentially by molecular flow through a small hole in a thin diaphragm. For certain applications a properly designed capillary leak has also proved useful (*3*). One method of constructing a diaphragm leak has been described by Honig (*1*). We have devised a different technique which seems to be suitable for making a number of relatively uniform diaphragm leaks. Several of these have been prepared and installed in the gas inlet system of a Nier-type mass spectrometer.

The procedure used in making the diaphragm leaks is as follows: One end of a number of 5-cm lengths of 7-mm Pyrex tubing is turned in a medium oxygen flame until the tube is nearly closed and only a very fine capillary (0.02–0.04 mm in diameter) remains through the thickened end. While the end is still hot and workable, a loose-fitting carbon rod is inserted into the open end of the tube. The constricted end of the tube is gently

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