

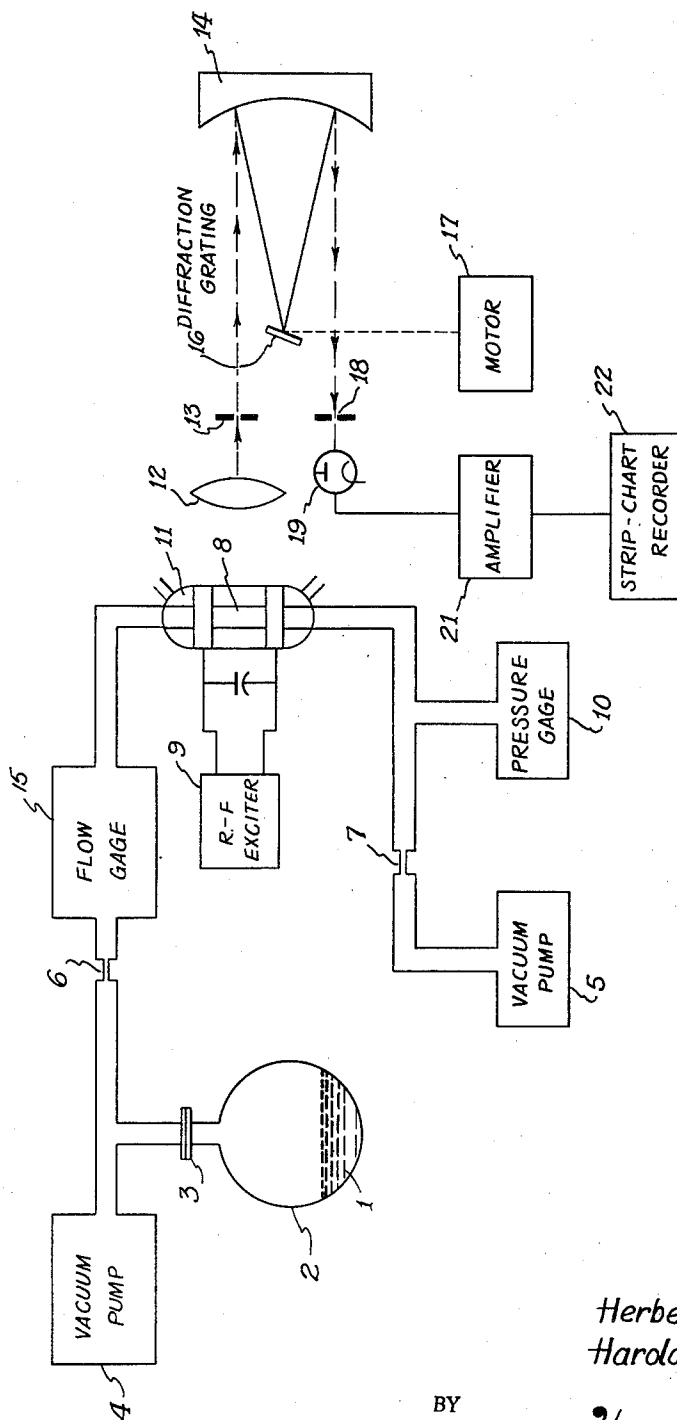
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RAPID SPECTROSCOPIC DETERMINATION OF TOTAL WATER CONTENT

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RAPID SPECTROSCOPIC DETERMINATION OF TOTAL WATER CONTENT

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(Granted under Title 35, U. S. Code (1952), sec. 266)

The invention described herein may be manufactured and used by or for the Government of the United States for governmental purposes without the payment to me of any royalty thereon, in accordance with the provisions of 35 United States Code (1952), section 266.

This invention concerns the problem of determining the total water content—water present in free, absorbed, hydrated, and/or bound form—of various materials. This is a problem of great commercial and practical importance. For instance, millions of bushels of corn and other cereal products are sold annually on terms that take moisture content into consideration. The textile and cement industries, among others, also have important problems of water content determination. But until now there has been no easy and rapid way of determining total water content. The present invention provides a quick, simple method of determining with high precision the water content of practically any substance. A known amount of the substance is immersed in a mixture of hydrogen and deuterium oxides; rapid spectroscopic determination of the ratio of these two oxides in the solution gives a measure of the water content of the substance.

The classic general method of determining water content is by weight loss. A sample is heated to a room temperature high enough to drive off the water and is kept there until its weight levels off. But when this method is used to determine the water content of corn, for instance, a hundred hours or more may be required for a determination. Even then, the accuracy of the determination leaves much to be desired.

More recently, some determinations of water content have been made by mixing the sample with heavy water and analyzing the resulting solution for deuterium-hydrogen ratio by means of a mass spectrometer. Although this method gives higher precision than the weight-loss method, it is still very slow and requires more elaborate equipment than the method of the present invention.

Accuracy to within $\frac{1}{10}$ of one percent of the true water content can be obtained by the method of the present invention. This accuracy is obtained even when the water content is small. For example, if the water content is only one percent of the total weight of the substance, the determination will be accurate to one part in 100,000 of the total weight of the substance. Such a determination can be made in a total time of one hour or less. If this high a degree of accuracy is not required, a determination of 3 percent accuracy can be made in about 7 minutes.

The first object of the present invention is to provide a rapid and accurate method for the determination of total water content of substances.

Another object is to provide a new, more convenient, more practical method for water-content determinations required in industry and commerce.

Another object is to provide new, more convenient, methods for tracer studies, using stable isotopes instead of radioactive isotopes.

Other uses and advantages of the invention will become

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apparent upon reference to the specification and drawing.

The figure shows a preferred form of equipment for use in water content determinations by the method of the invention.

To make a water content determination, a sample of the material to be investigated is mixed with a solvent consisting of deuterium oxide or, more conveniently, with a measured volume of deuterium-oxide—hydrogen-oxide mixture containing about 99 percent of deuterium oxide. The resulting solution contains water (hydrogen oxide) from the sample, and by comparing the D_2O to H_2O ratio of this resulting solution with the D_2O to H_2O ratio of the original solvent the water content of the sample can be readily calculated.

If the molar ratio of the hydrogen oxide to deuterium oxide in the original solvent is r , and the final molar ratio of the solution is R , then the fraction, f by weight of the sample which is water is given to a first approximation by the relation

$$f = \frac{(R-r)V}{(1+R)M}$$

where V is the volume of the solvent in milliliters and M is the weight of the original sample in grams. The approximation, which is good to about 4 parts in 1000, is introduced by assuming that the partial molar volumes of hydrogen oxide and deuterium oxide are the same, and that the density of water in the range of room temperature is 1,000.

The values of R and r are obtained by means of the apparatus shown in the figure. Briefly, what this apparatus does is to flow vapor from a deuterium-oxide—hydrogen-oxide mixture through an electrodeless discharge tube at reduced pressure. Light emitted by the vapor in this tube, when the vapor is excited by radio-frequency energy, is analyzed by means of a recording spectrometer.

Referring to the drawing, the deuterium-oxide—hydrogen-oxide mixture 1 to be analyzed is placed in a flask 2 which can be quickly connected to, or removed from, the rest of the system by means of connector 3. Air is removed by means of a suitable vacuum pump 4. Vapor from flask 2 flows through capillary constriction 6, flow gage 15, electrodeless discharge tube 8, and capillary constriction 7, where it is exhausted by vacuum pump 5. Constrictions 6 and 7 serve to control the flow of vapor through tube 8 as well as the pressure in tube 8. Pressure gage 10 indicates the pressure in tube 8. Fixed pressures in the range of 0.3 and 1.0 mm. of mercury have been found satisfactory. The vapor in tube 8 is excited by placing tube 8 in a field of radio-frequency energy generated by an R.-F. exciter 9. Tube 8 is provided with a water jacket 11 for cooling.

It is important for accuracy that the vapor in the discharge tube flow continuously during the analysis, so that only fresh vapor is analyzed at all times. If the vapor in the tube is closed off, the percentage of deuterium tends to change with time.

The analysis depends on the wave-length separation of the emission lines of hydrogen and deuterium due to the isotopic shift. The ratio of hydrogen to deuterium can be determined by measuring the ratio of the H_β line (4861.3 A.) to the D_β line (4860.0 A.) coming from the discharge. Vapor in the discharge dissociates into H and OH and D and OD, and the observed ratio of the intensity of the hydrogen to the deuterium line will be a measure of the ratio of hydrogen oxide to deuterium oxide. It has been established that the ratio of excited hydrogen to deuterium is proportional to the ratio of the concentration of hydrogen oxide vapor to deuterium oxide vapor.

Still referring to the drawing, light from tube 8 passes through condensing lens 12 and entrance slit 13.

to spherical mirror 14. Mirror 14 reflects the light to diffraction grating 16; a grating ruled 12,000 lines per centimeter has given satisfactory results. Grating 16 is slowly rotated by motor 17, and suitable speed-reduction gearing if needed. Monochromatic light from grating 16 is reflected by mirror 14 to exit slit 18. Photomultiplier tube 19 responds to the monochromatic light passing through exit slit 18. The electrical output of photomultiplier tube 19 is amplified by direct-current amplifier 21 and fed to strip-chart recorder 22.

With this arrangement, by rotating grating 16 to scan the desired portion of the spectrum, a graphic recording showing the amplitudes of the H_β and D_β lines can be obtained in about 20 seconds.

In the table below are given experimental results obtained with the method of the present invention when analyzing three different samples. It can be seen from this table that the experimental and theoretical results are in close agreement. Therefore the present invention provides a highly accurate as well as a very rapid method for determining the total water content of bodies.

Experimental determination of total hydration

Material	Hydrate gram (M)	Solvent, ml. (V)	Solvent Ratio Hydrogen to Deuterium (r)	Solution Ratio Hydrogen to Deuterium (R)	Experimental Hydration with standard Deviation of Mean (f)	Theoretical Hydration
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0.770	1.00	0.011	0.286	0.354 ± 0.003	0.361
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	0.648	1.00	0.011	0.249	0.364 ± 0.003	0.363
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	0.779	1.00	0.011	0.289	0.353 ± 0.003	0.363

The method of the invention does not depend on observation of the H_β and D_β spectral lines mentioned above. Any pair of spectral lines can be observed, provided that one of them is characteristic of deuterium and the other of hydrogen. The lines observed may be characteristic of molecules, including D_2O and H_2O , as well as of atoms. Other spectro-analytic means than those described can be used.

What is claimed is:

1. The method of determining the total water content of a substance the steps of which comprise mixing a sample of the substance with a solvent containing

deuterium oxide and spectroanalyzing the resulting solution to determine the relative proportions of deuterium oxide and hydrogen oxide present in said solution.

2. The invention according to claim 1 in which said solvent comprises a mixture of deuterium oxide and hydrogen oxide.

3. The invention according to claim 1 in which said solvent comprises a mixture of deuterium oxide and hydrogen oxide in known proportions, at least 50 percent by weight of said mixture being deuterium oxide.

4. The invention according to claim 1 in which said spectro-analyzing comprises subjecting vapor from said solution, at reduced pressure, to radio-frequency excitation, said vapor being flowed continuously through the region in which it is subjected to said radio-frequency excitation; resolving the light emitted by said vapor when thus excited into monochromatic light; and measuring photoelectrically the intensities of at least one spectral line indicative of the presence of deuterium and at least one spectral line indicative of the presence of hydrogen.

5. The invention according to claim 4, said reduced

pressure being maintained at a uniform value in the range of from 0.3 mm. to 1.0 mm. of mercury.

6. The invention according to claim 4, said radio-frequency energy having a frequency in the range of 100 megacycles to 10,000 megacycles.

7. The invention according to claim 4 in which said measuring comprises measuring the intensities of the H_β spectral line of approximately 4861.3 Angstroms wavelength and the D_β spectral line of approximately 4860.0 Angstroms wavelength.

No references cited.