by the U. S. P. On the other hand the increase in acidity of the various commercial products shown in Table I, shows that most manufacturers have not yet been able to control the uncertain factors which effect the stability of hydrogen peroxide, and the consequent increase in acidity.

The cause of the increased acidity must be due to a disintegration of the benzene nucleins of the acetanilid. In several cases the increase is much greater than can be accounted for by simple hydrolysis of acetic acid from the acetanilid.

The objection to a high acidity for hydrogen peroxide rests upon its use as a mouth wash. The organic acids formed by the oxidation of the preservative will exert no deleterious effect upon the teeth, and it is with the original mineral acidity alone that we are concerned. However, our present knowledge of the matter affords us no practical means of distinguishing between the two.

SCIENTIFIC LABORATORY OF PARKE, DAVIS & CO., DETROIT, MICH., June 28, 1915.

DISCUSSION.

Mr. Scoville: The point is these gentlemen have shown that when acetanilid is employed, in the decomposition which ultimately follows, there is more acid formed. We know that acetanilid has the temporary effect of a preservative agent. But the time comes when the hydrogen peroxide gets the best of it and decomposes the acetanilid itself, and then we have an odor and discoloration, which are the two objections to acetanilid as a preservative. They show the solution is more acid than it was before the acetanilid began to decompose; in other words, that excess of acidity in hydrogen peroxide solution does not necessarily mean that the excess has always been there; the acidity is partly formed by the decomposition of the acetanilid. Now, they don't give any recommendation or any definite explanation of that. They simply give a number of tables showing the facts, the acidity being determined when it was fresh and at the end of two years. Are there any questions on that?

Mr. Long: Do they figure out any possible reaction to account for the hydrolysis effect?

Mr. Scoville: They don't explain it; they have not attempted to give any explanation.

Mr. Long: Is it supposed to be acetic acid?

Mr. Scoville: Well, I should suppose so, but they do not say so.

Mr. Long: That is all I care to ask about.

RADIUM AND THE MEASUREMENT OF RADIUM EMANATIONS.

S. W. STRATTON, DIRECTOR OF THE BUREAU OF STANDARDS, WASHINGTON, D. C.

As practically all substances contain traces of radium, and consequently of radium emanation, the real problem that confronts the pharmacist and the physician is the determination of *how much* radium or radium emanation a preparation, or water, must contain in order that its therapeutic value may be appreciably affected thereby. If a lower limit to this quantity can be agreed upon, and if producers are required to state in *unambiguous units* the actual radium or radium emanation, content of their preparations, then the possibilities of successful fraud will be greatly limited.

As an example of the manner in which the use of ambiguous units assists the fraudulent, consider the "Mache unit" as a measure of radium emanation. This unit has been defined as that amount of radium emanation which when mixed with air will produce such a rate of ionization[1] of the latter that the saturation current[2] will be $\frac{1}{1000}$ of an electrostatic unit of current.

In order to measure this current the air and emanation must be enclosed in a vessel of some kind. It is evident that some of the alpha particles—these produce the ionization of the air—will strike the walls of the vessel and be there absorbed, thus being prevented from producing their full amount of ionization. Consequently the observed saturation current will be less than it would be were there no absorption by the walls. The percentage reduction thus caused in the saturation current is proportionate to the ratio of the total area of the walls to the total volume of the vessel. Whence it is evident that the observed saturation current corresponding to a specified amount of radium emanation will depend upon both the size and shape of the ionization chamber employed. The current alone does not suffice to define the amount of emanation; it is equally necessary to specify either the size and shape of the ionization chamber to which this current applies, or to specify that the observed current is to be corrected for the effect of the walls of the chamber. Since, whatever may be the shape of the chamber, the effect of the walls becomes ever less and less as the size of the chamber is made greater and greater, becoming exactly zero when the size of the chamber is indefinitely great, it is usual to speak of the value of the current after the correction for the walls has been applied as the saturation current in an infinitely large chamber. In actual practice large chambers are inexpedient as the voltage required to produce the saturation current in them is excessive. The correction that must be applied to the saturation current observed in any cylindrical vessel, of the kinds ordinarily used, in order to elminate the effect of the walls has been determined. For chambers of a common type this correction amounts to 30% of the current.

Some use the term "Mache unit" to denote that amount of emanation for which the saturation current *observed* in such a vessel is 1/1000 of an electrostatic unit; others use it to denote that amount for which the saturation current *after the correction* for the walls has been applied is 1/1000 of an electrostatic unit. The same term is used to denote two quantities which differ by 30%.

This is not all. The current that is observed depends upon how long the emanation has been in the vessel. When the emanation is first introduced, the current increases rapidly, then more slowly, becomes very nearly constant about five hours after the emanation is introduced and then very slowly decreases. Observers have differed as to the value of the current to use. Some have used the Mache unit to denote that amount which will give the specified current when the

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(1) When a gas is subjected to the radiations from radioactive substances some of its molecules are broken into two oppositely electrified portions. These charged portions are called ions; the process is spoken of as an ionization of the gas; and the vessel containing the gas that is being ionized is called the ionization vessel, or chamber.

(2) The electric current which passes through a given metallic conductor is directly proportional to the applied voltage; this, however, is not true of the current through a gas. In the latter case the current increases less rapidly than the voltage, and finally reaches a value beyond which it cannot be increased even though the applied voltage be increased many fold. This maximum current is known as the stauration current. The voltage required to produce the saturation current depends upon the rate of ionization of the gas, and upon the size and shape of the ionization chamber. The smaller the rate of ionization and the smaller the distance between electrodes of the ionization chamber, the smaller will this voltage be.

emanation is *first* introduced into the vessel; others have used it to denote that amount of emanation which, *when in equilibrium* with its products of disintegration, will give the specified current. *The first is nearly three times as much as the second.*

Although the best practice requires that this unit be defined in terms of the current produced by the emanation without its products of disintegration and in a vessel of infinite size, still the other uses are sufficiently numerous to protect one who desires to use them for fraud.

In the above the term "Mache unit" was used to denote the *amount* of radium emanation. It is frequently so used; but in its original use and as used by many it denotes a concentration of emanation. A water is said to have one Mache unit if the emanation *from one liter* of the water will, under specific conditions, produce a saturation current of 0.001 electrostatic unit.

Good authority can be found for both uses. Here again fraud is possible. If a bottle containing two liters of water is said to contain 2000 "Mache units," does this mean that *each liter* contains sufficient emanation to produce in air such an ionization that the saturation current under the specified conditions is 2000 x 0.001 electrostatic units; or is there only this much in the entire bottle?

All of this ambiguity can be avoided by the use of a carefully defined unit. Such a unit which has international sanction is the "curie." This is defined as the amount of emanation which can exist in equilibrium with one gram of radium (element). The latter is exactly defined by the International Radium Standard which is preserved in Paris, and with which the standard of this Bureau has been compared. One microcurie (=one millionth part of a curie) is approximately equal to 2700 times that amount of radium emanation which is designated by the "Mache unit" under its best sanctioned usage as a *unit of emanation.* Consequently one thousandth part of a microcurie (=one millimicrocurie) corresponds to 2.7 of these "Mache units."

Concentrations of emanation should be expressed in terms of *curies per liter.* Then a water containing 2.7 "Mache units," as used in the most approved sense as a *concentration unit,* would be said to contain one millimicrocurie per liter. If preferred, the expression "one thousandth of a microcurie" may be used instead of "one millimicrocurie."

There is likewise an indefiniteness in many statements referring to the use of sealed specimens of radium salts for gamma ray treatment. It is frequently stated that "so many milligrams of radium bromide," or "so much radium chloride," or "so much radium of such an activity," is used. This variation in the form of statement not only introduces confusion, but encourages fraud; especially is this true of the last.

Consider the last form first. The statement means that the tube contains the stated amount of salt and that an infinitely thin layer of a fair sample of this salt will, per gram of the salt, produce in a suitable alpha ray electroscope a saturation current that is a certain multiple of that produced per gram of uranium by an infinitely thin film of a uranium compound. Neither the weight of the salt in the tube, nor such a comparison can be made without opening the tube and removing the salt. Even then the comparison is not practical except for very low grade salt. In practice it is never attempted.

By very careful work the activity, as defined above, that is to be expected from a salt containing a given percentage of radium has been determined to a certain low order of precision. From this work we can compute approximately the amount of radium that a tube said to contain "so much radium of such an activity" should contain. By gamma-ray measurements, which can be made without opening the tube, the total radium content of the tube can be determined. *In no case that has come to the attention of this Bureau has the actual radium content of such a tube been nearly so great as was to be expected from the stated amount and activity of the salt.*

As the dealer makes no claim regarding the amount of radium the tube contains, the establishment of fraud upon the basis of this discrepancy would be impossible. Owing to the difficulties involved in the direct measurement of the activity, and to uncertainties somewhat similar to those mentioned in speaking of the "Mache unit," the establishment of fraud even by a direct study of the "activity" of the salt would be most difficult. Such a study would also be very expensive, in fact out of all proportion to the value of any such tube that has come to our attention.

Consider now the first two forms of expression which were mentioned. Both radium bromide and radium chloride exist in two forms, viz., the anhydrous and the crystalline. The terms "radium bromide" and "radium chloride," unless further qualified, may be applied with equal justification to either salt. The crystallized bromide contains 8.5% less radium than the anhydrous; and the crystallized chloride contains 10.7% less than the anhydrous. When the price of radium is considered and one takes into consideration the fact that it is solely the radium that gives value to the salt, these differences are well worth considering.

In at least one case that has come to the attention of this Bureau the purchaser specified that he was to receive so many milligrams of radium bromide. He did not realize that there were two bromides, and even after the tubes were delivered and paid for he did not know which bromide they were supposed to contain. In this case the uncertainty regarding the amount of radium he should have received amounted to about $300.00.

All such uncertainty can be avoided and the work of different men can be readily intercompared if all will express the content of each tube or preparation, and require the dealers to guarantee the content of all tubes and preparations in terms of the number of milligrams of radium (element) contained in them. The basis should of course, be the International Radium Standard.

It is also most desirable that the term "milligrams of radium" be used in all cases to denote solely the amount of the chemical element radium that is contained in the tube, or preparation. "Radium" is the name of a definite chemical element and its use as an abbreviation for "a radium salt" or for "a preparation containing radium" not only fails to conform to the recognized usage of chemical terms, but also introduces confusion.

Anything you or your committee can do to bring about the universal adoption of the International Units (the "curie" and the "milligram of radium"), and the precise use of the word "radium" will be of great service to all concerned.

THE MEASUREMENT OF RADIUM EMANATION.

Method: The measurement of radium emanation is based upon the fact that, when it is mixed with air, the alpha radiation from the emanation and its products of disintegration ionize the air and thus make it a conductor of electricity.

Other things being the same, the rate of this ionization is directly proportional to the amount of radium emanation present, and thus may be used as a measure of the latter.

The maximum current that can be passed through a given gas is called its saturation current; it is a direct measure of the rate of ionization of the gas, and can be measured in various ways. The simplest method is to determine the rate at which an insulated charged body loses its charge when immersed in the gas. In current practice the leaf of an electroscope is made a part of the charged body, and the rate of loss of charge is measured by the rate of fall of the leaf. If the leaf is timed always over the same portion of its path the observed rates will be proportional to the current through the gas, and, therefore, proportional to the rate of ionization.

Ions are being continually produced in a gas even when no radium emanation is present. The observed rate of fall of the leaf of the electroscope (often spoken of as the drift of the leaf) measures the total rate of production of ions, and, consequently, is greater than it would be were no ions produced except by the emanation present. It must, therefore, be diminished by the drift that is produced by what we may call the natural rate of ionization of the air, before it can be used as a direct measure of the amount of emanation present. The drift that is observed when there is no emanation present is known as the "blank drift" of the instrument. It includes the effect of any slight leakage of electricity over the insulating supports, as well as the leakage due to the natural ionization of the air.

When air mixed with radium emanation is filtered through a plug of absorbent cotton and admitted to a vessel which had previously been partially exhausted, the emanation itself is at first the only radioactive element present. However, it immediately begins to disintegrate with the formation of a series of other radioactive elements. The alpha radiation from these also ionizes the air and so the ionization at first increases rapidly with the time. The products of disintegration, being themselves radioactive, are continually disintegrating and so a time arrives when they have accumulated to such an extent that their rate of disintegration just equals the rate at which they are formed; they are then in transient equilibrium with the amount of emanation then present. After this they decrease in amount at the same rate as the emanation itself decreases from decay, equilibrium being always maintained.

Consequently the rate of ionization of the air in the vessel at first increases rapidly, then more slowly, and after about three hours becomes, and for some time remains sensibly constant. After this it slowly decreases, at the rate of a decrease of one-half in 3.85 days.

Owing to this variation in the ionization it is advisable to take all measurements at the same time after the admission of the emanation; it is best to choose this time as three to three and three-fourth hours, for then a practically steady state has been reached and a slight difference in the times will produce no error.

In order to be able to derive from the corrected drift of the leaf the amount of emanation introduced into the vessel it is necessary to know the corrected drift which corresponds to a known amount of emanation. This depends upon the particular instrument and its adjustment and may be determined by an experimental standardization. It also depends upon the density of the air in the ionization chamber; variations in the density of the atmosphere at a given place will seldom cause changes of over 5% in the observed current and the actual amount can be readily computed.[3]

So far only the case of emanation mixed with air has been considered. If the emanation is dissolved in water or other liquid, or absorbed in a solid it must first be quantitatively removed and mixed with a suitable volume of air and then measured as described above. Boltwood has shown that radium emanation can be completely removed from water by vigorous boiling.

Units. The only unit of emanation sanctioned by the International Radium Congress is the "Curie." This is defined as the amount of radium emanation which can exist in equilibrium with one gram of radium (element).

Submultiples of this unit are designated by prefixes as in the case of other metric units. The more important of these submultiples are given in the following table.

Designation	Emanation in equilibrium with
1 curie	1 gram of radium
1 millicurie=0.001 curie	1 milligram of radium
1 microcurie=0.000001 curie	1 microgram of radium
1 millimicrocurie=0.000000001 curie	1 millimicrogram of radium

The prefix "micro," meaning small, has long been in common use in electrical measurements to denote the one millionth part of the unit. A suitable, and common abbreviation for it is the Greek letter *mu* (μ); hence μ might be used as an abbreviation for micro curie, and $m\mu c$ for millimicrocurie.

One millimicrocurie is equal to 2.7 times the amount of emanation designated by the more common of the numerous "Mache units." The latter term having been used in several senses, and being unsanctioned by the International Congresses should be discarded. In fact Mache himself thoroughly disapproves of its general use.

Apparatus: The apparatus needed includes: (1) A suitable electroscope with attached ionization chamber which can be exhausted and then filled with the gas under test; (2) A microscope for reading the position of the leaf of the electro-

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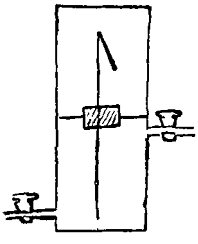
(3) Duane has shown that the relation between the value I of the saturation current observed in a cylindrical ionization chamber three hours after the introduction of the radium emanation is related to the value Ic that would have been observed had the walls produced no effect, in the manner shown by the equation

$$I = I_c\ (1 - 0.572\ S/V)$$

where V is the volume of the ionization chamber and S is its internal superficial area. The coefficient 0.572 applies to air at 15° C. and 760 mm. pressure, it varies inversely as the density of the air.

scope, as means must be provided for securely fastening this microscope in a suitable position fixed with reference to the electroscope, it is advisable that it be attached to the electroscope itself; (3 A stop-watch for the determination of the rate of motion of the leaf of the electroscope; (4) A piece of sealing wax, or other means, for charging the electroscope; (5) A good aspirator, or other means, for partially exhausting the ionization chamber; (6) A standard of radium emanation; and (7) Apparatus suitable for removing and storing the gas contained in the water, or other preparation under test.



Frequently the leaf of the electroscope is in the ionization chamber itself, but there are many advantages in having it in a separate compartment entirely cut off from the ionization chamber; somewhat as shown in the sketch. If many measurements have to be made it is very desirable to have the two compartments separable so that the electroscope proper can be securely mounted and any one of several ionization chambers can be attached to it, as desired.

In the absence of a standard dilute solution of a radium salt, many observers have used for preparing standards of radium emanation specimens of pitchblendes, of which the uranium content has been carefully determined. Since the weight of the radium contained in any specimen of unaltered pitchblende has been shown[4] to be equal to 3.33×10^{-7} times the weight of the uranium, in the same specimen, the amount of radium can be calculated when the uranium content is known. If a known weight of this ore has been kept in a closed vessel for a month or longer, then the emanation in the vessel, and ore, will have come to equilibrium with the enclosed radium and consequently its amount will be known. If, now, without opening the vessel, the enclosed ore is treated chemically so as to be dissolved and thus to set free the emanation retained in it, all of the emanation will become mixed with the other gases in the vessel and it is now possible to transfer this known amount of emanation to any vessel we desire.

Whenever a standard radium solution is available its use is much to be preferred. Radium solution should be strongly acidulated with hydrochloric acid. After a volume of a solution containing a known amount of radium has been kept in a gas-tight vessel for a month or more the amount of emanation in the vessel will be that which is in equilibrium with the amount of radium enclosed. Simple boiling of the solution will drive all of the emanation out of the solution, and it can then be transferred as desired. If the vessel containing the solution is then closed and put aside the same amount of emanation will have again collected in it by the end of another month; and so on. If it is undesirable to wait for a month the amount of emanation that has accumulated up to a given time after closing the vessel can be calculated from the time constant of radium emanation.

This Bureau is prepared to supply such standards at $5.00 each.

Adjustment: The eyepiece of the microscope must be so adjusted that the scale of divisions in the microscope is in good focus. Then the microscope must be so adjusted that, when the electroscope is charged so that the leaf makes an angle of 30° or 40° with the vertical, the leaf is near the center of the field of the micro-

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(4) Heinmann and Markwald, Physik. Ztschr. 14 p. 303, 1913.

scope; and, when its charge is varied, remains in focus wherever it may be in the field. The scale of divisions and the leaf must both be in good focus at the same time. When this is the case a lateral motion of the eye will not cause an apparent motion of one with respect to the other.

Many trials may be necessary before a satisfactory adjustment is secured. Having secured this adjustment the microscope should be securely fastened with reference to the electroscope; and should not again be moved.

Standardization: (1) Determine the blank drift. To do this exhaust the ionization chamber and refill it with dried and filtered air drawn from out of doors. Do this several times. Then charge the electroscope so that the leaf stands near the center of the field of the microscope; and by means of the stop-watch determine the rate at which the leaf falls. This rate should be very slow. If it falls one division of the microscope scale in 5 minutes, then the rate of drift is 0.0033 divisions per second. This is called the "blank drift," or the natural drift of the leaf.

(2) Determine the drift when a known amount of emanation is in the ionization chamber. To do this, exhaust the ionization chamber and then fill it with the air and emanation from the emanation standard. and so much outside air as may be necessary to make the pressure inside the ionization chamber equal to that outside. All of this air should be dried and filtered. Close the ionization chamber and leave it for about 2½ hours.

At the end of this time charge the electroscope so that the leaf stands beyond the extreme end of the scale in the microscope. Keep it charged for a half an hour. Then, by means of the stop-watch, determine the time required for the leaf to drift from one end of the scale to the other. Then recharge the electroscope and repeat. This should be done several times.

Suppose that the number of divisions is 50, and the average time of drift is 1 min. 19.62 sec.; then the rate of drift is 0.628 divisions per second. This is the drift due to the presence of the emanation and its products plus the blank drift. Hence the drift due to the emanation and its products is 0.628-0.003 or 0.625 divisions per second. This may be called the "corrected drift."

If the emanation standard contains 4×10^{-9} gm. (i. e. 4 millimicrograms) of radium, and had been sealed for over a month, then it contained the equilibrium amount (4 millmicrocuries) of emanation; and, if no loss occurred during the transfer, this is the amount of emanation which was introduced into the ionization chamber.

Hence a corrected drift of 0.625 divisions per second at 3 hours after the introduction of the emanation corresponds to the introduction of 4 millimicrocuries of emanation; and a drift of 1 division per second corresponds to 6.40 millimicrocuries.

The ionization chamber should now be exhausted and refilled with dry, filtered, outside air. This should be repeated several times so as to sweep out thoroughly all traces of emanation. This ionization chamber should not be used again until the following day; this delay is necessary to allow the "active deposit" formed upon its interior to decay.

So long as the instrument remains absolutely unchanged the amount of emanation needed to produce a corrected drift of one division per second also remains unchanged. Owing, however, to experimental errors and to the possibility of unsuspected changes taking place in the instrument, the standardization should be repeated several times at the beginning of the work and then at intervals of a month or so even though no change in the apparatus is suspected. Of course, if a change is made or is suspected to have occurred, the apparatus should be again standardized before proceeding with the work.

Measurement of Emanation: (1) Determine the blank drift, as in the standardization. Suppose it is found to be 0.0050 divisions per second.

(2) By boiling, remove the air and emanation from a suitable volume of the water to be tested; collect it above hot water. The volume of water should be so chosen as to give a drift that can be readily timed. Let the collected gases stand for ten minutes to allow any thorium emanation present to decay. Then introduce it into the previously exhausted ionization chamber, as for standardization. After 3 hours determine the rate of drift of the leaf; suppose it is 1.005 division per second. Then the corrected drift is 1.000 division per second; and, consequently, the amount of radium emanation removed from the volume of water used is 6.40 millimicrocuries. Hence, if the volume of water used was 100 cc. the water contains 64.0 millimicrocuries per liter.

Remarks. It is necessary that the amount of emanation to be measured or an accurately known fraction of this amount, be introduced into the ionization chamber without loss. The timing of the leaf must be carefully done and the same portion of the leaf must be used in all observations. In the computations it is assumed that the voltage employed is sufficient to produce the maximum, or "saturation," current; under all practical conditions no appreciable error will result from a lack of saturation if the leaf makes an angle of 30° to 40° with the vertical when in the middle of the field of the microscope, provided that the ionization chamber is not over 10 cm. in diameter. It has also been assumed that the density of the air has been the same in all cases; if this is not true and an accuracy greater than 5% is desired the proper correction must be applied.

The most readily available articles dealing with this subject are probably the following:

B. B. Boltwood: On the radioactivity of natural waters: American Journal of Science (4) 18 pp. 378-387, 1904.

B. B. Boltwood: The Origin of Radium: Philosophical Magazine (6) 9 pp. 599-613, 1905.

H. Schlundt and R. B. Moore: Radio Activity of the Thermal Waters of Yellowstone National Park: Bull. 395, U. S. Geological Survey, 1909.