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HYDROFLUORIC ACID.[1]

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HYDROFLUORIC acid is always made by decomposing ground fluorspar with sulphuric acid in cast iron vessels and absorbing the resulting fumes of hydrofluoric acid in leaden vessels of varying construction, containing more or less water, according to the strength desired.

The commercial acid, containing forty to fifty-two per cent. hydrofluoric, is stored and shipped in lead vessels, or small quantities in gutta percha bottles. Weaker acid, of about thirty-five per cent. and less, can be stored for a limited time in wood and is sometimes shipped in barrels, usually oil barrels. In this country the so-called "chemically pure" acid is packed in ceresine bottles, which answer very well, but must be kept away from the Bunsen burner, as the melting point of the ceresine is low. In Europe the C. P. acid is shipped either in gutta percha or platinum bottles, but the acid takes up, in course of time, mineral and organic matter from the gutta percha and ceases to be C. P. Platinum bottles are the best, but require a heavy investment.

The impurities, which can hardly be avoided in manufacturing commercial hydrofluoric acid, and are therefore always present, are:

1. *Hydrofluosilicic Acid.*—This is the most important impurity,

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[1] Abstracted from a lecture before the chemical section of the Engineers Society of Western Pennsylvania, at Pittsburgh, February 28th, 1896. Communicated by the author.

not because it does any direct harm in the application of the acid, but because the fluorine combined with silica is perfectly useless. The source of the hydrofluosilicic acid is free or combined silica in the fluorspar, which is all dissolved and volatilized by the hydrofluoric acid. It seems almost impossible to obtain spar free from silica. American ground fluorspar contains usually about one and a half per cent.; samples of English spar, which I have tested, were even higher in silica, about three per cent., while six samples of German spar contained from one-tenth to seven-tenths per cent. silica. In the rapid determination of silica in fluorspar an analytical problem presents itself, which I have not yet solved to my satisfaction. I use the following extremely simple method :

One gram of ground fluorspar, in a platinum dish, with a small platinum spatula, is dried at about 130° C., weighed exactly, moistened with hydrofluoric acid, stirred with a spatula, evaporated to dryness on the water-bath ; this is repeated, then dried again at 130° C., and weighed. The difference I assume to be silica, which is only correct when free silica is present, but the spar may contain silicates, for instance clay; in that case a fluoride of aluminum would be formed, part of the weight of the silica would be replaced by the weight of the fluorine retained and the silica be found too low. If carbonates are present the error would not be great, for instance,

$$CaCO_3 \ (100) \text{ would give } CaF_2 \ (78),$$

and the silica be found too high. The presence of carbonate is, however, easily detected, and the carbonate can be removed with acetic acid. Galena is often present in small quantities and gives the spar a grayish or bluish color, in that case

$$PbS \ (239) \text{ would give } PbF_2 \ (245),$$

an error that would not be perceptible. This simple method, to which any careful boy can be drilled in a short time, is therefore likely to give quite accurate results.

The great damage done by silica in the spar is plainly shown by the following equation :

$$(1) \quad \underset{60}{SiO_2} + \underset{234}{3CaF_2} + \underset{294}{3H_2SO_4} = \underset{144}{SiF_4(HF)_2} + \underset{408}{3CaSO_4} + \underset{36}{2H_2O}.$$

For every part of silica about four parts of fluorspar and five parts of sulphuric acid are wasted, or expressing it in money value, for every per cent. of silica at least ten per cent. (four per cent. for spar and about seven per cent. for sulphuric acid) should be deducted from the value of the spar.

2. *Sulphuric Acid*, which is distilled over in small quantities out of the decomposing vessel, does no harm in the application of the hydrofluoric acid for etching glass or pickling iron. But in analyzing the acid it must be determined, otherwise it would be figured as hydrofluoric acid.

On evaporation and calcining, commercial acid should leave but a trace of non-volatile matter.

About five years ago, having made some hydrofluoric acid in an experimental apparatus, I was confronted with the inability to tell what I had made; that is, I could not find a method which would have enabled me to determine the composition in a reasonably short time.

The methed of determining quickly the percentage of a liquid by its specific gravity is of little value for two reasons, first, because the methods for determining the specific gravity of other liquids can only be used with modifications for hydrofluoric acid, as they involve the use of a glass instrument of some kind. A glass hydrometer can only be used a few times until the acid has ruined it; picnometers are out of the question; even the temperature of hydrofluoric acid cannot be determined directly with a thermometer, as soon as a glass thermometer is placed into the acid the mercury begins to rise from the heat evolved by the action of the acid on the glass. I use, therefore, a platinum hydrometer. A hydrometer made from pure silver would probably last a long time. I have seen one made out of German silver plated with silver, but the hydrofluoric acid got through the plating and ate numerous pinholes into the instrument.

The impurities mentioned above, *i. e.*, hydrofluosilicic acid and sulphuric acid, influence the specific gravity of the hydrofluoric acid to a marked degree, so much that the determination of the specific gravity of an acid of unknown origin is of little value, but for controlling the process in the works, where the character of the raw materials and the degree of purity of the produced hydrofluoric acid is known, it is of value, provided the conclusions drawn from it are from time to time verified by an analysis. It will not do to depend too much on the specific gravity.

Without taking up any time with a description of the experiments, which led finally to the method I use, I will give the latter in detail.

The samples are brought to the laboratory in lead cylinders of convenient size, with a handle. These are placed in water of 15° C., often remaining there for at least five minutes; the specific gravity is taken ; then with the aid of a small platinum tube, serving as a pipette, and chips of filtering paper, to remove a small excess, three portions are weighed out :

1. Two grams in a very small platinum crucible (holding about five cc).
2. Two grams in a large platinum crucible (holding about forty cc.)
3. Four grams in a small platinum dish.

A. TOTAL ACIDITY.

Place the small platinum crucible, covered with its lid, in a large platinum dish (holding about 100 cc.), then run, according to the expected percentage, twenty-five or fifty cc. normal caustic solution (forty grams caustic soda per liter) from a pipette into the dish, upset the covered crucible, and mix the acid and alkali with a platinum stirrer; add two drops of a solution of phenolphthalein (1 gram in 100 cc. alcohol) and then add more of the normal soda solution from a burette till the colorless liquid assumes the characteristic bright red color. Place over a Bunsen burner and heat to about 50° C ; the red color will disappear. Finally add normal solution from the burette slowly till the red color remains constant when heated, which indicates that all free sulphuric acid, hydrofluoric acid, and hydrofluosilicic acid have been neutralized. The number of cubic centimeters used we call "*a*."

If litmus is used in place of phenolphthalein, the soda solution has to be added till the color is perfectly blue, but the end of the reaction is indistinct, while with phenolphthalein as indicator it is very sharp.

B. HYDROFLUOSILICIC ACID.

To the acid in the large platinum crucible (two grams) add five cc. water (measured approximately), then slowly about two grams[1] potassium carbonate either in small pieces or in concentrated solution, add about fifteen cc. of fifty per cent. alcohol and then as many cubic centimeters of ninety-five per cent alcohol as water used, which will bring the whole to a volume of about twenty-five cc. containing about fifty per cent. alcohol,[2] let it stand for at least one hour. Filter[3] and wash the gelatinous precipitate, consisting of potassium silicofluoride, with fifty per cent. alcohol till blue litmus paper ceases to be turned red by the filtrate. Throw the filter with the precipitate into a platinum dish, add about twenty-five cc. of water and warm to about 50° C., titrate slowly with normal caustic soda solution and phenolphthalein, as described in the determination of total acidity. The number of cubic centimeters used we call "*b*."

C. SULPHURIC ACID.

Place the platinum dish containing four grams of the acid to be tested, on a water-bath under a hood with a good draft and evaporate till acid fumes have completely ceased to be given off. Titrate the remaining syrupy liquid, which contains the free sulphuric acid, cold, with normal acid solution, using either litmus or phenolphthalein as indicator. The number of cubic centimeters used we call "*c*."

The reactions involved are as follows:

$$\underset{20}{HF} + \underset{40}{NaOH} = \underset{42}{NaF} + \underset{18}{H_2O}. \tag{2}$$

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[1] The amount of potassium carbonate is calculated to neutralize the acids only partly. To avoid an excess it is advisable to test the liquid with litmus paper, which should show a strong acid reaction. But there should be at least enough potash to form potassium silicofluoride with the fluosilicic acid. In analyzing acid of entirely unknown composition I take for every cubic centimeter normal soda solution used for the determination of total acidity 0.05 gram potassium carbonate. Potassium chloride might be used in place of the carbonate, but in that case free hydrochloric acid is formed, in which the potassium silicofluoride is somewhat soluble.

[2] If the liquid contains more than fifty per cent. alcohol, potassium fluoride is precipitated, if much less alcohol, potassium silicofluoride may remain in solution.

[3] I use a platinum funnel because glass funnels are acted on, but that does not influence the accuracy of the method.

$$(3)\quad \underset{144}{SiF_4(HF)_2} + \underset{240}{6NaOH} = \underset{252}{6NaF} + \underset{60}{SiO_2} + \underset{72}{4H_2O}.$$

$$(4)\quad \underset{220}{SiF_4(KF)_2} + \underset{160}{4NaOH} = \underset{168}{4NaF} + \underset{116}{2KF} + \underset{60}{SiO_2} + \underset{36}{2H_2O}.$$

$$(5)\quad \underset{98}{H_2SO_4} + \underset{80}{2NaOH} = \underset{142}{Na_2SO_4} + \underset{36}{2H_2O}.$$

Now the number of cubic centimeters of normal soda solution used in the first titration and called "a" represents the alkali necessary to neutralize the hydrofluoric acid, hydrofluosilicic acid, and sulphuric acid, and in order to find the number of cubic centimeters used for hydrofluoric acid alone, we have to subtract those used for hydrofluosilicic acid and sulphuric acid, but although we used the same weight (two grams) for the determination of the hydrofluosilicic acid, it would not be correct to subtract the number of cubic centimeters used, because in the potassium silicofluoride two atoms of fluorine are neutralized and we only neutralize with normal solution the remaining four atoms, which are combined with silicon. It would therefore have required $b + \frac{b}{2}$ cc. to neutralize the free acid.

Having employed four grams of substance for the determination of the sulphuric acid, the number of cubic centimeters used for that determination must be divided by 2. The number of cubic centimeters used for hydrofluoric acid alone are therefore equal to $a - (\frac{3}{2}b + \frac{c}{2})$ and as each cubic centimeter normal solution indicates 0.020 gram HF and two grams of substance have been used, the number of cubic centimeters found by the above formula express, without further calculation, the percentage of free hydrofluoric acid. Therefore

$$a - (\tfrac{3}{2}b + \tfrac{c}{2}) = \text{per cent. free hydrofluoric acid.}$$

After the foregoing explanation the calculation of the percentage of hydrofluoric acid is an easy matter. One cc. normal sodium hydroxide indicates 0.055 gram potassium silicofluoride, which was obtained from 0.036 fluosilicic acid; having used two grams of substance, 0.036 has to be divided by 2 and multiplied by 100 to get the percentage, or

$$b \times 1.8 = \text{per cent. hydrofluosilicic acid.}$$

The percentage of free sulphuric acid is obtained by multiplying c, the number of cubic centimeters used, by 0.048, dividing by 4 and multiplying by 100, or

$$c \times 1.2 = \text{per cent. free sulphuric acid.}$$

Other free acids, muriatic or nitric acid, which influence the accuracy of the determination, are not likely to occur in commercial hydrofluoric acid and their presence can easily be detected by well-known analytical methods:

To give an idea of the composition of some of the makes of hydrofluoric acid, I have appended a few of the analyses made in the course of five years:

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Specific gravity......	...	1.299	1.264	1.253	1.244	1.264	1.282	1.247	1.234
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Hydrofluoric acid....	39.6	42.2	44.3	48.1	48.6	51.1	54.2	48.6	33.5
Hydrofluosilicic acid.	2.7	14.9	10.1	4.7	5.0	6.8	8.1	6.3	10.6
Free sulphuric acid..	...	0.8	0.8	4.0	1.9	1.4	1.2	0.8	1.6

1. Oct. 1891. Baker & Adamson, C. P. acid in ceresine bottle, 0.005 per cent. non-volatile residue.
2. Oct. 1891. Manufactured by J. C. Wiarda, sample received.
3. Nov. 1891. " " " " sample taken from package of 100 pounds.
4. Jan. 1892. Manufactured by James Irwin & Co., sample of lot of 3500 pounds.
5. Mar. 1892. Manufactured by James Irwin & Co., sample of lot of 3400 pounds.
6. Jan. 1894. Manufactured by Bender & Aldred, sample taken from package of 100 pounds.
7. Jan. 1895. Manufactured by James Irwin & Co., sample taken from tank holding 3000 pounds.
8. Oct. 1895. Manufactured by James Irwin & Co., sample taken from tank holding 3200 pounds, 0.015 per cent. non-volatile residue.
9. Jan. 1896. So-called "pickling acid" sample received from a foundry.

By comparing analyses Nos. 2 and 7 it can be seen what influence hydrofluosilicic acid has in raising the specific gravity; although No. 2 has a higher specific gravity than No. 7, it contains twelve per cent. less hydrofluoric acid, but six and eight-tenths per cent. more hydrofluosilicic acid. Nos. 3 and 6 have the same specific gravity, but No. 6 contains six and eight-tenths per cent more hydrofluoric acid and three and there-tenths per cent. less hydrofluosilicic acid. The influence of sulphuric acid on the specific gravity can be seen by comparing Nos. 4 and 5.

A great difficulty in the manufacture of hydrofluoric acid is the very disagreeable and dangerous nature of the gaseous and liquid acid. The effects of the fumes on the respiratory organs are more injurious than those of other acids. Still more marked are the effects of the liquid acid on the skin. One drop of acid, although it does not make itself felt for a few hours, will, even on the horny skin of a workman's hand, cause a very painful inflammation in one-half day. Against the fumes the workmen protect themselves by respirators, or by the simpler way, which they usually prefer, of tying a handkerchief over nose and mouth and by greasing the unprotected parts of the face with lanolin. The latter is as effective as vaseline and easier to wash off. Against liquid acid rubber gloves afford protection. If liquid acid comes in contact with the skin it should be washed off at once with water and aqua ammonia, or another alkali, which will prevent injury.

In conclusion, I wish to say a few words about the different applications of commercial hydrofluoric acid.

The oldest, and up to the present time, most extensive application is for etching glass. For this purpose it can be applied in three different ways. In the gaseous form by suspending the articles to be etched over a mixture of fluorspar and sulphuric acid. This is the oldest way of etching and I believe most burettes, graduated cylinders, etc., for laboratory use are still marked in this way. If applied in gaseous form the acid leaves the surface opaque, while the liquid acid leaves the surface smooth and transparent. For the production of an opaque surface with liquid acid many empirical formulas are published and every glass factory, or rather every etching boss, has his own secret formula. But they all aim to produce a mixture of hydrofluoric acid with a fluoride of ammonium, or potassium, or sodium, with which a number of other substances such as sulphuric, acetic, or muriatic acids, or ammonium or potassium sulphate, etc., are mixed, but it seems quite unnecessarily. Hydrofluoric acid prepared for etching opaque goes under the trade name of "white acid." Lead glass is very rapidly and uniformly etched and acid of forty-five to forty-eight per cent. is usually employed, while lime glass requires a stronger acid and more time. Lately, acid as strong as fifty-two per cent. HF is employed. "White acid" is much more convenient for application than gaseous acid and acts very rapidly; for instance, a lead glass lamp chimney can be rendered opaque by simply dipping it into the acid for one minute. Lime glass,. even with acid specially prepared for it, requires about two minutes immersion. It is important that the temperature of the acid and the glass should be about 15° C. Parts of the glass which are to remain unetched, must be protected. For this purpose a number of substances are in use. Asphaltum varnish is usually employed, when the design is printed on paper and then transferred to the glass; for the so-called needle work a mixture of Burgundy pitch and beeswax is used.

A more recent application of hydrofluoric acid is for cleaning castings from sand. These have so far been cleaned, either by mechanical means, or with sulphuric acid, but the first is expensive and neither way, in many cases, satisfactory. The sulphuric acid loosens the sand by dissolving the iron to which it is attached, while hydrofluoric acid dissolves the sand itself and therefore acts more promptly and does not cause any loss of iron. It also dissolves the magnetic oxide formed on the surface of the iron very readily, much more so than sulphuric acid. This latter point is important for castings, which have to be worked afterwards with edged tools, the magnetic oxide being very hard. For cleaning castings, the acid is diluted to about one or two per cent. HF, the pickling can therefore be carried on in wooden vessels.

Some of the firms, who use hydrofluoric acid for cleaning iron, have kindly sent me reports on it. The most interesting parts of these reports I will mention here with their permission:

Mr. S. H. Stupakoff, Supt. Union Switch and Signal Co., writes:

"We use the acid in the proportion of two and one-half quarts to one-half barrel water, containing about twenty-five gallons," —(equal to one pound forty-eight per cent. hydrofluoric acid in thirty-five pounds of water, the liquid would therefore contain one and four tenths per cent. HF)—" The bath is filled to the top with castings and they are left in it for about half an hour. We can renew our charge by adding each time one quart of acid.

" We find that the hydrofluoric acid is vastly superior to sulphuric acid, as the latter will not pickle satisfactorily in less than one day, and besides this we use about double the quantity of sulphuric acid compared with hydrofluoric acid to pickle the same amount of castings."—(as the quantities given by Mr. Stupakoff are by volume, this would be equal to one pound of ninety-three per cent. sulphuric acid in eleven pounds of water, the liquid would therefore contain eight and a half per cent. sulphuric acid, or six times as much as the hydrofluoric acid bath.)

"With the sulphuric acid we experienced a great deal of trouble by obtaining a white sediment on the castings, which was very difficult to remove, even when washed in hot water. This white coating would frequently work through the paint, with which the castings were subsequently covered.

" We had no occasion to try this acid for cleaning any other material but cast iron, with the exception of one instance, when we tried to remove heavy coatings of rust from a lot of mixed material, consisting of cast iron and wrought iron. The hydrofluoric acid did this to perfection and left a perfectly bright surface.

"I can say, in conclusion, that I am perfectly satisfied, that the use of hydrofluoric acid for the cleaning of new castings and corroded iron is certainly a success, and I will always prefer it to the old method of pickling in sulphuric acid."

From the engineer of another firm I received the following report:

" The best solution is one to thirty" —(this is by volume, and the bath would contain, as he used forty-eight per cent. hydrofluoric acid about two per cent. HF)—" As we make no small castings of gray iron I have only used the acid on maleable castings, with the result that small castings are cleaned excellently in two hours. I have also cleaned castings in a mixture of one acid to fifty water"—(the bath would contain about one per cent. HF)—" by leaving them in over night, but we prefer to clean with the stronger acid. The pickling vat is usually filled up with castings three times before it requires more acid.

" It takes sulphuric acid twice as long with the same proportion"—(that is, one to thirty would give a solution of about five and six-tenths per cent. sulphuric acid)—"and then does not eat into the corners as well as hydrofluoric acid; also wastes more iron and does not leave it bright."

For iron which is to be enameled, the cleaning with hydrofluoric acid is also advantageous, because it leaves a purer metallic surface than can be obtained with other acids.

I am informed that a large firm in this city is at present making arrangements with a view of throwing out their whole mechanical cleaning plant, in which they have been cleaning sixty tons a day.

Hydrofluoric acid or its salts are also used in distilleries to insure a more complete fermentation.[1]

The latest application, of which I heard only a few days ago, is for cleaning out oil and gas wells. It seems that the shooting of a well sometimes packs the rock so tightly that the hole is dryer after the shooting than before. By pouring about six barrels of hydrofluoric acid (I suppose the acid is used diluted) into the hole, which dissolves the silicates and afterwards is pumped out again, gas or oil get an outlet.

NITROGEN ASSIMILATION IN THE COTTON PLANT.

BY CHARLES E. COATES AND W. R. DODSON.

Received March 3, 1896.

IN the spring of 1895, while looking up the literature of the cotton plant, it was noted that no quantitative work could be found touching the question of nitrogen assimilation in any member of the mallow family. As the cotton plant is highly nitrogenous in character and as there seemed to be no reason why the leguminoseae should have a prëemption claim on the absorption of free nitrogen, it was decided to undertake certain experiments along these lines, following Hellriegel's methods as far as possible, in the hope that something of importance might

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[1] Article of Dr. Leo Backeland, this Journal, 14, 212.