various distilled ester fractions and the residue were fractionally crystallized from ethyl alcohol. The identity of the individual acids which were separated by this means was established in each case by their melting points and by observing whether or not these melting points were lowered when they were mixed with equal quantities of the respective acids, the composition of which had been determined by elementary analysis. In no instance was there observed any depression of the melting point.

As no myristic acid could be isolated from fraction 1, 100 grams of the unsaturated acids were esterified and fractionally distilled under diminished pressure. The acids were recovered from the first fraction and submitted to fractional crystallization from ethyl alcohol, but no myristic acid was obtained. However, a very small quantity of palmitic acid was isolated and identified.

Palmitic acid was separated from the first three saturated ester fractions, stearic acid from fractions 3 and 4, and lignoceric acid from fraction 5 and the residue.

The acids isolated from the fractions in each case confirmed the deductions previously made from the mean molecular weights of the saturated acid esters.

The composition of the oil in terms of glycerides is given in Table III.

TABLE III

The Percentages of the Fatty Acids as Glycerides

Glycerides of	Per Cent
Oleic acid	63.3
Linoleic acid	31.2
Palmitic acid	2.6
Stearic acid	1.1
Lignoceric acid	.05

Summary

The characteristics and the percentages of the fatty acids present in apricot kernel oil as glycerides have been determined. The oil studied was found to contain about 90.6 per cent of unsaturated acids consisting of a mixture of oleic and linoleic acids. The saturated acids amounted to about 3.6 per cent and were composed almost entirely of palmitic and stearic acids.

Mention is made of the utilization of the press cake for the recovery of volatile oil, for fertilizer, and as a feed for livestock. An analysis of the press cake is given. A table of the smoking points for various fats and oils by the J. M. McCoy procedure is given for comparison with that of apricot kernel oil.

In addition to the established use of the oil by cosmetic manufacturers, other possible outlets include its use as a salad and cooking oil, for the roasting of shelled nuts, and for the manufacture of soap.

Selenium: The New Catalyst in Kjeldahl Digestions

By M. F. Lauro

Ammonia determinations are everyday occurrences in the laboratory of the oil chemist, since he must analyze not only the oil content of seed and nut, but also the cake and meal left from their expression or extraction, in order to ascertain their commercial value as feed and fertilizer. Hence, an article on this subject should not be out of place in the program before the American Oil Chemists' Society.

It is common knowledge that concentrated sulphuric acid will break down the complicated structure of both animal and vegetable proteins into the simpler ammonia compound, which the chemists can more readily act upon and determine, recalculating to the original protein, than attempt to separate the protein as such or obtain by other means. Considerable charring takes place in the process of conversion to simpler forms necessitating the addition of more acid and a prolonged period of digestion before final clearance to a colorless solution. The sulphates of either soda or potash are added with the idea of so raising the boiling point as to keep the mixture liquid and prevent undue loss of acid, and thereby, with a minimum amount of acid, hasten the process to its conclusion. To still further accelerate the reaction, small amounts of either mercury or copper are used. They act catalytically and cut down the time to a matter of hours where it took practically all day in the original Kjeldahl process.

Copper was always popular with cereal chemists, because of its convenience, cheapness and the fact that it indicated by change of color the excess of lye necessary to add for the next step of distilling the ammonia from the ammonium sulphate formed in digestion. Mercury became the favorite of the oil chemist, as he dealt with a greater variety of mixed materials, more complex in nature and in addition containing greater oil content. With these substances it was found in general that the mercury compounds gave more concordant and slightly higher results. The chief objections to mercury lay in the need for its precipitation with sodium or potassium sulphide before distillation, and in the occasional low results from prolonged digestion and consequent decrease in sulphuric acid, whereby a very stable amino-derivative of mercury is formed. Whenever this is suspected the addition of a little more acid and further digestion will break it up, otherwise precipitation with sulphide and subsequent distilling will not give all of the ammonia.

There has been no change in the method for a great many years. Improvement has proceeded rather along the line of standardizing the procedure, in developing new types of flasks and apparati and in the change from gas to electric heater. This has helped cut down the time appreciably, so that, in general, it may be safe to say that flour may be digested completely in about an hour's time, cottonseed meal in about two hours, and other material such as meat and fish scrap in from two to three hours.

The need for more rapid digestions, however, never abated. The time factor is a most important one not only in commercial laboratories but in control mill work. Research to cut down the time still further, was therefore never wanting.

The prevailing idea favored the noble metals as catalysts, in spite of their cost. Hence the search for a new catalyst was almost exclusively restricted to them. Most of the author's previous attempts, except for nickel, lay in that special class of elements.

But logic sometimes plays peculiar tricks. Your true scientist reasons out a conclusion by à priori thinking; the inventor usually achieves his result by hit and miss method with, however, a one-tracked idea. Quite often what happens is, that in working out a problem logically, we may stumble on a discovery collaterally. Others then call this a stroke of luck, but is it? It would seem to me that such an apparent accident is actually created out of circumstances as a by-product of research, which but for that research would possibly never have happened.

So it was with this new catalyst, selenium. It may be said that I stumbled upon it, when as a matter of fact, I had been working on and off for some ten years prior to its popping into my mind while on work of an entirely different character than protein determination.

Selenium is not a noble metal. It isn't even a metal, but an element on the border line with the properties closely akin to sulphur. Strange to say, neither sulphur nor tellurium react catalytically. Therefore a priori logic was against it.

The occasion for its discovery is instructive. While separating the oxides of tantalum and columbium from each other, the method of H. B. Merrill was used. This required extraction with selenium oxychloride, a fuming and corrosive liquid with unique solvent powers. At the same time I was running a long line of Kjeldahl digestions, some of which were clearing off more slowly than others, when the idea suddenly suggested itself to make use of the oxychloride. The thought was more from the standpoint of oxidation than that selenium itself would hasten the process. A drop or two added to the dark digestion mixtures cleared them off in a matter of minutes. Later, selenium obtained from the waste acids of the Merrill method was tried, achieving the same quick results. A purchased sample failed to react as rapidly as freshly precipitated selenium indicating variation in activity.

This modification of the Kjeldahl process has served to cut down the total time by at least one-half. In the beginning, 0.2 gram was used for each test in place of copper or mercury, the other reagents being the same as in the standard methods. It was found that 0.1 gram selenium was ample, and the sulphate of soda may be cut down to eight grams instead of ten. I have found as little as 0.05 grams of selenium sufficient. Too much renders the end-point a little difficult to ascertain, as a slight yellow color persists in the acid solution, and is unnecessary, anyway, as the time of digestion is not appreciably affected.

The cost is insignificant, as at two dollars the pound, 0.1 gram selenium per determination means less than 0.05 cents, or less than one cent for twenty single tests.

A precipitant is of course unnecessary. The use of powdered zinc (30 mesh) is preferable to flocculent or mossy zinc to prevent bumping in distillation, as with the latter, some frothing is caused by the selenium reducing out of the solution. Whether, after its addition to the cooled digestion mixture, the selenium is completely removed from solution by zinc or not, is immaterial, except that there is a tendency to froth in the former case.

Combining the catalysts, as selenium with either copper or mercury shortens the time slightly in the case of copper and appreciably when mercury is used, but here again we have the question of convenience and in the latter instance that of precipitation, to contend with. Selenium by itself does the digestion so well that it hardly seems worth the bother to add the others.

The thirty check samples which the Society sends out to the many chemists throughout the country have been analyzed by the writer in accordance with the modified method and the results obtained agree very closely to those by the official method. Likewise, samples of check flours sent by the American Association of Cereal Chemists, New York Section, were similarly analyzed with figures in close agreement with the official copper method. In all cases, the selenium method was much the faster.

Since the author's short paper of April 1931, a number of publications by others have appeared, confirming the conclusions contained therein and in addition have brought out some interesting applications of their own. There is therefore no particular reason for tabulating results to show any comparison of methods. However, a brief resumé of the literature to date might not be improper or irrelvant.

R. M. Sandstedt of the Agricultural Experiment Station, Lincoln, Neb., ran a series of tests on high protein flour and on bran, using the three methods, 0.1 gm. copper, 0.7 gm. mercuric oxide and 0.1 gm. selenium. The selenium acted more rapidly in digestion than the copper and at about the same rate as the mercury, being complete with the use of gas burners in about forty-five minutes, clearance in thirty. He found the cost to be 0.15 cents for Se, 0.48 cents for HgO and 0.002 cents for Cu. He also stated that it appeared there was greater danger of losing nitrogen by extremely long digestion with Se than with the other catalysts.

C. E. Rich of Robin Hood Mills, Saskatchewan, Canada, used the oxychloride of selenium together with copper and obtained results one-half hour sooner than with copper alone. Clearance was had in less than 15 minutes while copper took 35 minutes. Digestion was complete in 30 minutes with Se, while Cu took about an hour. The combination accelerated the reaction more than either alone.

H. C. Messman, Enid Terminal Elevator Co., Enid, Okla., combined mercury, copper and selenium and found digestion of flour and wheat complete in from 15 to 20 minutes, thus making it possible to do a complete nitrogen determination in less than one hour with the use of electric heaters. He employed 8 grams per test of flux made up of 90 parts sodium sulphate, 7 parts mercuric sulphate, 1½ of copper sulphate and 1½ of metallic selenium. The cost of selenium used was less than one-quarter of one cent per test, saving in current consumption alone more than offsetting this cost.

H. E. Crossley in the Journal of the Society of Chemical Industry, wrote that he applied the use of selenium in the digestion of coal. In one case he used a mixture of 11 parts mercuric oxide and 89 of potassium sulphate, and in another case, a mixture of 2 parts selenium and 98 of the sulphate. Disappearance of char took place after 87 minutes in the first instance and only 33 minutes in the second. Complete digestion required of course more time. He concluded that the time of digestion was shortened appreciably with the use of selenium and the cost of catalyst reduced.

J. Tennant, H. L. Harrell and A. Stull of the New York Hospital, N. Y., adopted the selenium modification of the Kjeldahl process in place of Cu in a variety of extracts tested in the Allergy Clinic, such as of pollens, guinea pig epithelium, and urine, etc. They obtained checking results with a decrease in time of one-half to two-thirds.

E. S. West and A. L. Brandon, Washington University School of Medicine, St. Louis, Mo., used the oxychloride of selenium in improving the Koch-McMeekin peroxide micro-Kjeldahl method for the determination of nitrogen in organic compounds and biological fluids, as urine, blood filtrates, cystine, phenacetin, etc. They used 1 cc. of a digestive mixture for each determination, which itself contained only 1 cc. of the oxychloride made up to 500 cc. The cost was therefore insignificant, being about 4.5 cents for 500 ccs. of digestion mixture. There was much less tendency to bump when selenium was used, and results were more consistent. Combined with sucrose, it was more effective on resistant compounds like creatine and creatinine than the peroxide method, which does not yield up all the nitrogen of the compounds. Selenium, also, did not interfere with subsequent nesslerization.

A few more papers are in the process of publication, indicating the widespread interest this new catalyst has aroused.