from CHF_2CCl_3. In no case was the fluorination reaction accompanied by loss of hydrogen chloride or hydrogen fluoride and consequently no ethylenic by-product was found. There was usually no tar formation, but a very small quantity was formed in the worst cases, when reagents of "technical" grade were employed.

Summary

A method of fluorination is described which consists in passing a stream of hydrogen fluoride through a mixture of the substance to be fluorinated and mercuric oxide. Practical directions are given for obtaining good yields and for a simple method of recovering the mercury.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICS, HARVARD UNIVERSITY]

Variations in the Relative Abundances of the Isotopes of Common Lead from Various Sources

BY ALFRED O. NIER[1]

Because of the apparently constant atomic weight of common or ore lead, the assumption usually has been made that its isotopic composition also is constant. Whereas several isolated isotopic analyses of common lead have been made, there is no record of any systematic study having been undertaken for the purpose of checking the constancy of the relative abundances. In the present work twelve samples were studied with a mass spectrometer and considerable variations were found. The investigation is of particular interest, as the specimens examined vary greatly in both geologic age and geographic origin. Moreover, of the twelve samples, nine have had chemical atomic weight determinations made on them—all in the same laboratory.

Apparatus and Procedure.—The mass spectrometer used for obtaining the results to be presented here already has been described.[2] Positive ions of lead are formed by the collision of electrons with lead iodide vapor. The ions are drawn out of the region where they are formed, are accelerated and sent around a 180° magnetic analyzer where the ion currents are measured with an electrometer tube amplifier.

During an analysis, the portion of the tube containing the semicircular analyzer is kept at room temperature. The part where the ions are formed is held around 400°, and the side-tube from which the lead iodide vapor diffuses into the ionizing region is maintained at approximately 300°, the exact temperature depending on the pressure desired in the ionizing region. In actual practice, this pressure was between 10^{-4} and 10^{-5} mm. The amount of material needed for an analysis is very small. During a typical run, where no attempt was made to economize on material, less than 13 mg. of lead iodide, *i. e.*, less than 6 mg. of lead, was consumed. With reasonable care it should be possible to obtain reliable results on 1 mg. of lead.

The procedure in making an analysis was as follows: the sample to be studied was attached in the evening and the mass spectrometer tube evacuated and baked overnight in order thoroughly to out-gas it. Measurements were taken the next morning and afternoon. The side-tube containing the sample was removed and the mass spectrometer was again baked overnight, this time to remove the lead iodide. The following morning the apparatus was baked for several hours with iodine vapor flowing through it to combine with any metallic lead deposited in the tube from the thermal decomposition of lead iodide. Baking of the tube continued until late in the evening in order to remove the remaining traces of lead iodide. A new sample could then be attached and the procedure repeated. It is seen that an analysis may be performed every two days. Actually, in one case, fifteen samples were examined in thirty-four consecutive days.

Because of the careful treatment of the apparatus between samples, described above, the relative abundances of the isotopes obtained for a given specimen did not depend upon the previous history of the apparatus. That is to say, there was no contamination due to previous samples. In fact, one even could change from a sample of ordinary lead to one of radiogenic lead and then back again to the ordinary lead and reproduce the original results exactly.

The lead iodide was prepared by precipitation

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(1) National Research Fellow.

(2) Nier, *Phys. Rev.*, **52**, 933 (1937).

from a solution of the nitrate (in a few cases from the chloride) with a solution of sodium iodide, washing and drying. Since the groups $I^{127}Br^{79}$ and $I^{127}Br^{81}$ have the same masses as two of the isotopes of lead, the iodine from which the iodide was prepared was carefully freed from bromine, as well as chlorine.

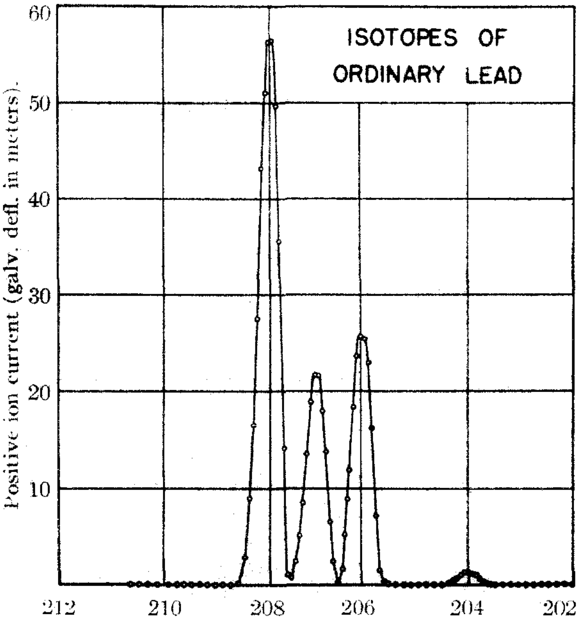

Fig. 1.—Mass spectrum showing the isotopes of common lead. Positive ion current expressed in terms of cm. deflection of galvanometer at its highest sensitivity. One cm. represents about 2.5×10^{-15} ampere.

Results

Preliminary reports on the results to be presented here have already been given.[3] A typical mass spectrum obtained is shown in Fig. 1. The relative abundances of the isotopes are assumed to be proportional to the relative heights of the positive ion current peaks. This assumption is justified in view of the fact that the relative heights as measured were found to be independent of variable conditions in the tube, such as electron current, pressure, etc. As a further check upon any possible discrimination in the apparatus, mercury vapor was admitted occasionally, and the Hg^{198}/Hg^{204} abundance ratio measured under conditions similar to those employed while the lead measurements were being taken. At no time was this ratio found to differ appreciably from that previously given.[2]

Figure 2 gives the lower part of Fig. 1 in greater detail. It can be seen from this that Pb^{204} produces a very definite peak that can be measured with nearly the same accuracy as the other peaks. Inasmuch as the apparatus was thoroughly baked and liquid air used on the traps, the height of the Hg^{204} peak is negligible, since even Hg^{202}, which exists with over four times the abundance of Hg^{204}, cannot be discerned in Fig. 2. In addition, no traces appear of the isotopes Pb^{210}, Pb^{209}, Pb^{205}, and Pb^{203}, at one time reported by Aston[4] with abundances indicated by the horizontal lines above the corresponding mass number position. Later, Aston[5] withdrew these isotopes in view of the fact that in a number of elements his rarer isotopes were found to be of a spurious origin. In particular, Bainbridge and Jordan[6] showed that Pb^{209} could not exist with even one-tenth the abundance originally claimed for it by Aston. That the withdrawal of the other rare lead isotopes was justified is shown by the present work. It is now possible to say that if Pb^{210}, Pb^{209}, Pb^{205}, and Pb^{203} exist, it must be with abundances less than $^1/_{100}$, $^1/_{1000}$, $^1/_3$, and $^1/_{20}$ of those originally given by Aston.

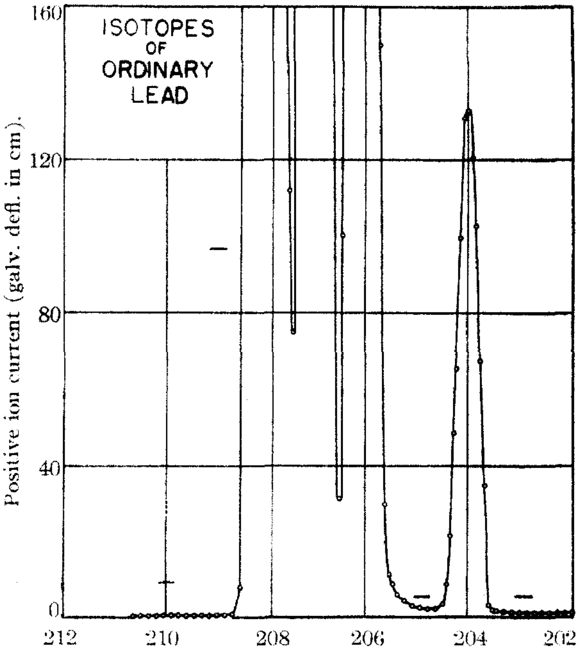

Fig. 2.—Lower portion of Fig. 1, drawn with enlarged ordinate scale.

Columns 4, 5, 6, and 7 of Table I give the relative abundances of the isotopes found for twelve samples of lead varying vastly in both geologic

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(3) Nier, *Phys. Rev.*, **51**, 1007 (1937); **53**, 680 (1938).

(4) Aston, *Proc. Roy. Soc.* (London), **A140**, 535 (1933).

(5) Aston, *Nature*, **137**, 613 (1936).

(6) Bainbridge and Jordan, *Phys. Rev.*, **50**, 282 (1936).

TABLE I

No.	Source of lead, locality	Geological age (in m. y.)	Isotope abundances				Excess			Excess		Mean mass number	Atomic weight	
			204	206	207	208	206	207	208	$\frac{207}{206}$	$\frac{208}{206}$		Physical	Chemical
1	Galena	Pre-Cambrian	1.000	15.93	15.30	35.3						207.243	207.218[a]	207.206[b]
	Great Bear Lake	1300												
2	Galena	Pre-Cambrian	1.000	16.07	15.40	35.5						207.242	207.217	
	Broken Hill, N. S. W.	950												
3	Cerussite	Pre-Cambrian	1.000	15.92	15.30	35.3						207.242	207.217	207.21[c]
	Broken Hill, N. S. W.	950	1.000	15.93	15.28	35.2						207.241	207.216	
4	Galena	Late Pre-Cambrian	1.000	18.43	15.61	38.2	2.50	0.31	2.9	0.12	1.16	207.229	207.204	207.209[d]
	Yancey Co., N. C.	600												
5	Galena	Carboniferous	1.000	18.10	15.57	37.85	2.17	.27	2.55	.12	1.17	207.231	207.206	207.21[c]
	Nassau, Germany	240												
6	Cerussite	Carboniferous	1.000	18.20	15.46	37.7	2.27	.16	2.4	.070	1.06	207.228	207.203	207.20[c]
	Eifel, Germany	240												
7	Galena I	Late Carboniferous	1.000	21.65	15.88	40.8	5.72	.58	5.5	.10	0.96	207.203	207.178	207.22[c]
	Joplin, Mo.	230												
8	Galena II	Late Carboniferous	1.000	21.60	15.73	40.3	5.69	.44	5.07	.077	.89	207.200	207.175	
	Joplin, Mo.	230	1.000	21.65	15.75	40.45						207.200	207.175	
9	Galena	Late Cretaceous	1.000	19.30	15.73	39.5	3.37	.43	4.2	.127	1.25	207.228	207.203	207.21[c]
	Metalline Falls, Wash.	80												
10	Cerussite	Late Cretaceous	1.000	15.98	15.08	35.07						207.239	207.214	207.21[c,e]
	Wallace, Idaho	80	1.000	16.10	15.13	35.45						207.242	207.217	
11	Wulfenite & Vanadinite	Miocene	1.000	18.40	15.53	38.1	2.47	.23	2.8	.093	1.13	207.229	207.204	207.22[c]
	Tucson Mts., Arizona	25												
12	Galena[f]		1.000	17.34	15.47	37.45	1.43	.15	2.07	.105	1.45	207.240	207.215	
	Saxony, Germany		1.000	17.38	15.44	37.3						207.238	207.213	
								Average		.10	1.13			

[a] Sample calculation: 207.218 = 207.243 × (1 + 1.55 × 10^{-4})/1.000275. [b] Marble, THIS JOURNAL, **59**, 653 (1937). [c] Baxter and Grover, *ibid.*, **37**, 1027 (1915). [d] Baxter and Alter, *ibid.*, **57**, 467 (1935). [e] Baxter, Faull and Tuemmler, *ibid.*, **59**, 702 (1937). [f] Sample 12 was obtained from Dr. A. V. Grosse, of the University of Chicago, who believed it to be a sample of galena from Saxony, Germany.

age and geographic origin. The abundance of 204 has been chosen arbitrarily as a reference, as it is not produced, as far as is known, by radioactive decay. An examination of the results reveals that variations occur in the relative abundances with different samples. These variations lie outside the possible experimental errors, as is evidenced by the fact that with the four samples where analyses were repeated the agreement was within at least one per cent. The probable error in the measurements is of the order of 0.5%.

In the last two columns of Table I are given the atomic weights as determined by the physical and chemical methods. In computing the atomic weight from the physical data, the mean mass number is first calculated from the relative abundances. The result so obtained is converted to the chemical scale as follows. The conversion factor in going from the physical to the chemical scale is taken as 1.000275.[7] The packing fraction of lead was found by Aston[4] to be between 0 and +1.0, whereas a value of +2.0, or greater, is deduced from Dempster's[8] data. In computing the atomic weight from the physical data, a packing fraction of +1.55 is chosen arbitrarily, as it brings the physical and

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(7) Hahn, *Ber.*, **71**, 1 (1938).

(8) Dempster, *Phys. Rev.*, **53**, 64 (1938).

chemical values into the best possible agreement.

Table II gives the results of previous investigators as well as the results obtained by the writer for his two extreme samples, numbers 1 and 7. All abundances are given in percentages for the sake of comparison. In view of the relatively large variations reported in the present work, no serious discrepancies exist between the work of the various experimenters. It should be mentioned, however, that the measurements on Pb^{204} here reported are the only accurate ones obtained to date.

TABLE II

	208	207	206	204	Mean mass number
Aston[4]	50.1	20.1	28.3	1.5	207.173
Rose and Stranathan[9]	51.5	21.3	26.3	0.8	207.228
Mattauch[10]	52.95	21.35	24.55	1.15	207.25
Nier, Sample 1	52.29	22.64	23.59	1.48	207.243
Nier, Sample 7	51.43	20.00	27.31	1.26	207.203

Discussion

An examination of the variations shows that they are definitely not of a random nature; those samples which contain relatively more Pb^{206} also contain relatively more Pb^{207} and Pb^{208}. Within the experimental errors samples 1, 2, 3, and 10 have the same isotopic constitution and also contain the least amounts of Pb^{206}, Pb^{207}, and Pb^{208}. The fact suggests that one consider the other samples as made up of this kind of lead plus contaminations of uranium lead (Pb^{206} and Pb^{207}) and thorium lead (Pb^{208}). For want of a better name for the lead low in Pb^{206}, Pb^{207}, and Pb^{208}, one may call it "uncontaminated" lead. As the three oldest samples have the isotopic constitution of "uncontaminated" lead there is a strong temptation to identify it tentatively with primeval lead—that is, lead as it existed when the earth's crust formed. The discovery of a sample of common lead containing less Pb^{206}, Pb^{207}, and Pb^{208} might force one to make a quantitative change in the argument to be presented here, but it seems doubtful that one will be found which differs enough to compel one to make a qualitative change.

Samples 1, 2, and 3 will thus be considered tentatively as "uncontaminated" lead. In columns 8, 9, and 10 are then recorded the excess amounts of 206, 207, and 208, *i. e.*, radiogenic contamination, for the other "contaminated" samples. The isotopic constitution of sample 1 is arbitrarily chosen as that for "uncontaminated" lead in making the subtraction. Thus, the amount of excess 206 for sample 4 is obtained by subtracting 15.93 from 18.43, etc. The choice of sample 1 as typical "uncontaminated" lead is a rather unfortunate one in spite of the great age of this sample, as it came from the Great Bear Lake region (a source of uranium ores), and hence might possibly have become contaminated. However, this sample does contain as little 206, 207, and 208 as any of the others, so that the choice is as good a one as can be made at this time.

An examination of the amounts of excess isotopes reveals that the excess 208 is practically equal to the excess 206, whereas the excess 207 is approximately 10% of the excess 206 in each case, the averages for all the contaminated samples being, excess 208/206 = 1.13, excess 207/206 = 0.10. It should be mentioned that the minerals from which the lead was extracted were essentially free of thorium and uranium, and hence, in all probability, the contamination of the "uncontaminated" lead by radiogenic lead took place before the mineral was formed. In the case of the Joplin material, a rough calculation shows that if the excess isotopes were generated by thorium and uranium present as impurities in the galena, the amounts would have to be, respectively, *two and six times as great* as the total amount of lead present!

It is a common belief among many students of ore deposits that ore lead has its ultimate origin in the igneous rocks or the magmas of these rocks. If such is the case, one should expect it to consist of primeval lead contaminated by radiogenic lead, inasmuch as the igneous rocks are known to contain uranium and thorium, and, consequently, radiogenic lead as well as common lead.

The values found for the two ratios for excess isotopes are not at all unreasonable, as far as supporting the contamination hypothesis is concerned, in view of other information at our disposal. If one assumes the age of the earth to be around 2×10^9 years, and if one further assumes that the radiogenic lead appearing in the above samples was being formed during the time between the formation of the earth and the formation of the minerals, one may assume the average age of the radiogenic contaminations to be of the order of 1.5×10^9 years, the exact value assumed being quite immaterial. As the rate of decay of ura-

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(9) Rose and Stranathan, *Phys. Rev.*, **49**, 916 (1936).

(10) Mattauch, *Naturwissenschaften*, **25**, 763 (1937).

nium is approximately three times that of thorium, the Th/U ratio in the substance in which the radiogenic lead was formed then must have been $3 \times 1.13 = 3.4$. Due to the difference in the rates of decay of thorium and uranium, the Th/U ratio of such a source would be today $3.4/0.85 = 4.0$.

Holmes[11] assumes this ratio to lie between 1.6 and 2.4 for igneous rocks. Evans and Raitt[12] believe the value to be considerably higher, possibly between 5 and 10. Finney and Evans[13] give values between 3.2 and 10.6, with an average of about 7. The Pb^{208}/Pb^{206} ratios found by the writer for the excess lead are thus not inconsistent with the view that ore lead is a concentration from igneous rocks or the magmas of such rocks.

The ratio of excess $Pb^{207}/Pb^{206} = 0.10$ lends further support to this hypothesis, as it is roughly of the right order of magnitude for old uranium lead. An actual calculation using new data available for the relative abundances of the uranium isotopes[14] indicates that for the uranium lead formed during the period between 2×10^9 and 5×10^8 years ago the Pb^{207}/Pb^{206} ratio would be approximately 0.14. In view of the fact that the numbers given in the column of excess Pb^{207} are obtained by subtracting two numbers very nearly equal, one can hardly expect better agreement. Moreover, this ratio depends in a somewhat critical way on what one assumes the isotopic constitution of primeval lead to be. The disagreement might well indicate that "uncontaminated" lead differs slightly from primeval lead.

In a recent paper, Holmes[11] makes use of the constancy of the atomic weight of common lead (and the alleged isotopic constancy) in an attempt to prove that it cannot be a concentration from granitic or basaltic rocks, or their respective magmas, but must have its origin in some deeper source in the earth. The present work shows definitely that the relative abundances of the isotopes of common lead do vary, but that the manner of variation is such as to have little effect upon the atomic weight. Moreover, the data are not inconsistent with the view that ore lead is related to ordinary igneous rocks, provided that one assumes the Th/U ratio in such rocks to be around 4.0, rather than 1.6 to 2.4 as is assumed by Holmes. Nine of the twelve samples studied by the writer were the *identical* samples which appear among those listed in Holmes' Table IV.

On a simple igneous rock derivation picture one should expect the oldest samples to contain a minimum of radiogenic lead contamination and the youngest a maximum. In this respect the data have some deficiencies which may or may not be of a serious nature. Except for the fact that the three oldest samples contain a minimum of apparent contamination there is no direct correlation between the age of the deposit and the amount of contamination. In fact, sample 10, a young mineral, has essentially the same isotopic constitution as the assumed "uncontaminated" lead. Such apparent difficulties may be only a manifestation of the fact that the total amounts of uranium and thorium in rocks vary greatly from specimen to specimen, and hence the proportion of radiogenic lead to ordinary lead in such specimens also varies quite independently of any variation with time.

In conclusion, the writer wishes to emphasize the fact that the explanation for the variations advanced in this paper is to be taken as tentative only. The accumulation of more data may lead the way to a better theory. However, with the information now available, the interpretation does seem to be reasonable and not in serious disagreement with any well established fact. An objection may be raised that the variations might be present in primeval lead itself. In answer to this, one can only say that the variations are much larger than any that have been reported for other elements (with the possible exception of hydrogen and a few other isolated cases, where the variations can be explained very easily by isotopic separation taking place in nature). It does not seem likely that the variations reported here can be due to isotopic separation, as one would expect them to be a monotonic function of the mass. The view entertained by some that common lead may be only a mixture of thorium and uranium leads generated since the earth's beginning certainly is not correct for at least two reasons, namely, (1) common lead contains Pb^{204} which apparently is not produced by the disintegration of uranium or thorium, and (2) the Pb^{207}/Pb^{206} ratio in common lead is far too high to be consistent with our knowledge of the relative rates of decay of the actinium and uranium series,

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(11) Holmes, *Economic Geol.*, **32**, 763 (1937).

(12) Evans and Raitt, *Phys. Rev.*, **48**, 171 (1935).

(13) Finney and Evans, *ibid.*, **48**, 503 (1935).

(14) Nier, Bulletin American Phys. Soc., Washington Meeting, 1938.

provided one assumes the age of the earth to be of the order of 2×10^9 years.

The writer wishes to express his appreciation to Professor G. P. Baxter of the Department of Chemistry, Harvard University, who very kindly prepared and furnished eleven of the twelve samples used. It was only through his interest and coöperation that this work was possible.

Summary

1. A mass spectrographic study of the isotopes of twelve samples of common lead shows that the relative abundances vary considerably in spite of a nearly constant atomic weight.

2. A tentative explanation for the variations is found if one arbitrarily considers some of the samples to be "uncontaminated" lead and the others "uncontaminated" lead to which has been added approximately equal quantities of uranium and thorium leads. As the minerals from which the lead was obtained are essentially free of thorium and uranium, such contamination probably took place before the mineral was formed.

3. A search for the isotopes Pb^{210}, Pb^{209}, Pb^{205}, and Pb^{203} indicated that if such isotopes exist at all they must exist with much lower abundances than was at one time supposed.

Cambridge, Mass. Received May 7, 1938

[Contribution from the School of Chemistry of the Institute of Technology of the University of Minnesota]

Studies on Aging and Properties of Precipitates. XXII. The Induced Precipitation of Mercuric Sulfide from Sodium Mercuric Sulfide Solutions by Zinc Sulfide. A New Case of Postprecipitation

By I. M. Kolthoff, Frank S. Griffith and D. Romund Moltzau

It was found by Feigl[1] that when a solution of a zinc salt is added to a solution of sodium mercuric sulfide under such conditions that the resulting liquid phase is not supersaturated with regard to mercuric sulfide, the precipitate which separates contains mercury and its color varies from white to yellow orange or brown, depending upon the amount of mercury in the precipitate. The mercury is not removed readily from the precipitate by extracting with sodium sulfide solutions. Moreover, Feigl found that the sulfides of cadmium, lead and manganese acted in a manner similar to zinc sulfide whereas the sulfides of silver, cupric and cuprous copper, ferrous and ferric iron, thallium, bismuth and cobalt did not induce the precipitation of mercuric sulfide from a sodium mercuric sulfide solution. In the present paper it is shown that the induced precipitation of mercuric sulfide by zinc sulfide is a phenomenon of postprecipitation. This case of postprecipitation is different from others[2] previously investigated in this Laboratory, in that the mercuric sulfide is taken up by the zinc sulfide from a solution which is *not supersaturated* with regard to the former. Such a postprecipitation will occur only when the following two conditions are fulfilled: (1) the postprecipitated substance is soluble in the primary precipitate or forms a compound with it; (2) the speed of separation of the primary precipitate is greater than that of the postprecipitated substance. If the former condition is not fulfilled no postprecipitation can occur from solutions which are not supersaturated with regard to the second precipitate. If the first condition is fulfilled but not the second a coprecipitation and not a postprecipitation will take place.

Materials Used

Zinc sulfate solutions were made from recrystallized c. p. chemicals. They were standardized against potassium ferrocyanide.[3]

Mercuric perchlorate solutions were made from reagent quality mercuric oxide and perchloric acid. A 0.05 *M* perchloric acid solution in equilibrium with mercuric oxide was found to be 0.004 *N* in free acid.

Sodium Sulfide.—The commercial products available were not suitable for the present work because of large amounts of impurities (thiosulfate). Therefore, the sodium sulfide solutions were made by passing washed hydrogen sulfide through a measured quantity of 5.30 *N* sodium hydroxide. A slight excess of hydrogen sulfide as measured by the increase in weight of the solution, was absorbed and the concentrated solution diluted with oxygen-free water. The solution was then analyzed for sulfide and total basicity and the appropriate amounts of

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[1] F. Feigl, *Z. anorg. allgem. Chem.*, **157**, 269 (1926).

[2] For a review see I. M. Kolthoff and D. R. Moltzau, *Chem. Rev.*, **17**, 293 (1935).

[3] I. M. Kolthoff and E. A. Pearson, *Ind. Eng. Chem., Anal. Ed.*, **4**, 147 (1932).