

**Determination of Trace Elements by Chemical Analysis
and Neutron Activation in Meteorites of the Collection
of the Viennese Museum of Natural History**

2nd Communication*

By

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With 8 Figures

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In the present paper a thorough analysis is described of six olivine-hypersthene chondrites, one pyroxene-plagioclase-achondrite, one medium and one coarse octahedrite as well as of an ataxite of high nickel content.

For the wet-chemical determination of the main constituents a rapid method of analysis has been developed which has been found to be very suitable. For the final determination of the elements methods based on chelatometric fluorescence titration in ultra-violet light are employed.

Also for the trace elements a separation method was developed which, at the present stage, allows the analysis of twelve elements in one operation. This separation technique is applicable after neutron activation and to isotopes with half lives exceeding 24 hours.

Based on the development of space research especially with respect to theories about the origin of the solar system and the cosmic abundance of the elements, meteoritic research has gained considerable importance.

From the collection of the Viennese Museum of Natural History ten meteorites have been investigated. They consisted of 6 olivine-hyper-

* This paper has been dedicated to Professor Dr. *Friedrich Wessely* on the occasion of his 70th birthday.

sthene-chondrites, 1 pyroxene-plagioclase-achondrite, 1 medium octahedrite, and 1 coarse octahedrite as well as 1 ataxite of high nickel content:

Moës (Roumania): Its fall was observed in 1882. 50 g of this meteorite have been made available for our investigations¹.

Holbrook (Arizona): Its fall was observed in 1912. The investigations were carried out on 6.0 g of this meteorite¹.

Sokobanya (Yugoslavia): Its fall was observed in 1877. For our investigations 11.7 g of this meteorite were employed. It should be mentioned here that the stone of Sokobanya together with several other meteorites of similar composition has been discerned by *Craig* in 1964 from the group of the olivine-hypersthene-chondrites (*L*-group*) and has been grouped into a *LL*-group. The overall iron content of these so called Sokobanyites corresponds to that of the *L*-group of chondrites, but nevertheless the portion of metallic nickel-iron in the former is lower². (The *H*-group** comprises the olivine-bronzites while the *L*-group consists of olivine-hypersthene-chondrites.)

Knyahinya (SSSR): Its fall was observed in 1866. Of this meteorite 2.6 g have been available for our investigations.

Long Island (Kansas): This meteorite has been found in 1891 and 2.1 g have been analysed.

Waconda (Kansas): This meteorite has been found in 1873. The investigations have been performed on a 4.80 g sample.

Stannern (ČSSR): Its fall was observed in 1808. This meteorite is one of the few pyroxene-plagioclase-achondrites which show a characteristic tuff-like appearance. The investigations have been carried out using 1.9 g of the meteorite sample.

Kenton County (Kentucky): This medium octahedrite has been found in 1889 and 2.4 g have been made available for our investigations.

Arva Magura (ČSSR): This coarse octahedrite has been found in 1840 and for our investigations 3 pieces of altogether 7 g have been available.

San Cristóbal (Chile): This ataxite of high nickel content has been found in 1882. For the investigations a 12 g sample has been at our disposal.

Sampling is one of the most difficult problems which is encountered in the chemical analysis of meteorites. This is due to the fact that a meteorite is „a priori“ a fraction which has been formed by random partitioning. Therefore the result of an analysis is only absolutely true with respect to the ratios in the material of the sample which has actually been used. Consequently generalizations drawn from the results can only be made with great care.

For the homogenisation of stony meteorites a *Retsch*-vibration mill (grinder) has been found to be very suitable. This mill is equipped with a 5 ml shaking vessel and balls consisting of agate. With this grinder the meteoritic samples are not contaminated by trace elements and consequently no erro-

* *L* = Low iron content.

** *H* = High iron content.

¹ W. Kiesel, *Z. anal. Chem.* **227**, 13 (1967).

² B. Mason, *American Museum Novitates* 2223 (1965).

neous results are obtained. Contamination may however occur if vessels are used which consist of steel or tungsten carbide³.

In these investigations iron meteorites show a behavior similar to that of steel samples. Their hardness and tensile strength make homogenisation difficult. In a ball mill made of aluminum oxide a fine powder in only a small amount is obtained. In a fraising-machine made of zirconium carbide which is driven by an air turbine not only abrasion may occur but it is also practically impossible to collect the fine chips which are distributed by the air jet. The use of other drilling- or fraising-tools involves that high alloy tool steels have to be employed which means that undesirable erosion of elements occurs. Because of these reasons the iron meteorites were cut by means of a thin steel saw. The slides thus obtained showed a thickness not exceeding 1 mm. This thickness of the slides should never be greater than 1.1 mm so that no erroneous results due to self-shielding during the neutron activation of the samples are obtained⁴. With a thickness of 1.1 mm the maximum change of flux in the sample does not exceed 1%.

For samples which are analyzed by wet-chemical means this restriction does of course not apply. In each case the sample fractions were cleaned in the following way. Firstly adhering oil and metal dust were washed off with reagent grade acetone and then possible contaminations introduced by the steel saw were removed by treating the samples for 30 to 40 seconds with warm 5 N hydrochloric acid (prepared from high purity hydrochloric acid of Merck Co and redistilled water). Finally the samples were washed with redistilled water followed by reagent grade acetone.

For the wet chemical analysis 700 to 900 mg of meteoritic material were found to be necessary while for the assay by neutron activation of selenium, arsenic, antimony, tin, rhenium, mercury, chromium, scandium, cobalt, zinc, gold, and iridium samples ranging from 90 to 140 mg were required. 500 mg samples were used for the non-destructive analysis and for the determination of trace elements having isotopes which show half-lives below 24 hours. From 150 to 200 mg were retained until the course of analysis was worked out which was required for those trace elements which on neutron activation give isotopes with half-lives exceeding 24 hours. For investigations by the microscope and by the electron beam micro probe amounts from 40 to 100 mg were available.

Wet Chemical Determination of Main Constituents

For the assay of the main constituents of meteorites we have developed a rapid and accurate working procedure. This method is based essentially on the techniques of ion exchange and liquid-liquid extraction, and the final determination of the various components is performed by fluorescence titration using EDTA as the reagent.

Working Procedure:

Analysis of Stony Meteorites: At least 650 mg of the finely ground material is weighed in a platinum crucible and is dried for 2 hours at 110° C in a drying

³ O. G. Koch und G. A. Koch-Dedić, Handbuch der Spurenanalyse, Berlin-Göttingen-Heidelberg: Springer 1964.

⁴ W. Schulze, Neutronenaktivierung als analytisches Hilfsmittel. (Die Chemische Analyse, Band 50.) Stuttgart: F. Enke 1962.

cupboard (water content). Subsequently 10 ml of 8 *N* HNO₃ are added and the mixture is evaporated to dryness on a water bath. To the residue 5 ml each of conc. nitric and 40% hydrofluoric acids are added in order to remove silica. This fuming with HF is repeated and then the sample is fumed to dryness on a sand bath with sulfuric acid. The residue is dissolved in 5 ml of 6 *N* HCl. This solution is transferred to a 100 ml beaker and the crucible is thoroughly rinsed. After the addition of 50 ml of hot water the solution is filtered through a very dense filter paper (blue ribbon) and the filtrate is evaporated to dryness on a water bath. The filter and residue is ashed in a platinum crucible and the residue thus obtained is evaporated to dryness after the addition of a mixture consisting of nitric and hydrofluoric acids. Subsequently insoluble Na₃AlF₆ is treated with 200 mg of boric acid at 1200° C over a period of 45 min. Then the crucible is rapidly cooled to allow an easy transference of the melt to a porcelain dish. Residues of the melt remaining in the platinum crucible are transferred to the dish rinsing the former three times with 10 ml each of methanol saturated with HCl. The excess of boric acid is removed by evaporation on a water bath in the presence of methanol saturated with HCl. The residue is taken up with 5 ml of 6 *N* HCl, the solution is diluted to 50 ml with hot water and filtered. Both filtrates are combined and evaporated to dryness. The residue is taken up with 100 to 150 ml of 7 *N* HCl. This solution is passed through an anion exchange column of 2 cm inner diameter and 20 cm in height (filled with the anion exchanger Dowex 1, X 8, 100 to 200 mesh), using a flow rate of 4 ml/min. Non-adsorbable components of the solution are removed by a subsequent washing with 150 ml of 7 *N* HCl. The effluent contains Ni, Mn, Al, Cr, alkaline earth metals, and alkali metals. Adsorbed Co is eluted with 150 ml of 5 *N* HCl. Subsequently iron is removed with 300 ml of 0.5 *N* HCl. Both elements are collected separately and the volume is considerably reduced on the water bath. To the fraction containing the Co 2 g of NH₄Cl are added, making it alkaline by addition of 5 ml of an ammonia-ammonium chloride buffer solution of pH 10. The Co content is determined by fluorescence titration with an EDTA-solution (solution 1) using Fluorexone as the indicator and an ultra-violet lamp as the light source. The solution is transferred to a measuring flask and in an aliquot portion of this solution Fe is determined by titration with an EDTA solution (solution 2). This titration is carried out at a pH of 2 to 2.5 using sulfosalicylic acid as the indicator.

The volume of effluent is reduced by evaporation on a water bath and to the solution 5 g NH₄Cl are added. After addition of 1 g of hydroxylamine hydrochloride Al and Cr are precipitated with NH₃ solution. The precipitate is filtered off, dissolved in warm dilute HCl and both elements are reprecipitated in the same way. The hydroxides of Al and Cr are dissolved on the filter by warm 3 *N* HCl, the volume of the solution being reduced by evaporation. Then its pH is adjusted to about 2 by the addition of a solution of NaOH. Then 0.5 ml of glacial acetic acid is added and the pH of the solution is adjusted to 3.4 using sodium acetate. After addition of 3 drops of a 0.002% solution of morine in methanol, EDTA-solution (solution 2) is added from a burette until the green fluorescence of the solution which is observed under an ultra-violet lamp has faded. Then about 3 ml of the EDTA-solution are added in excess. Subsequently the solution is rinsed into a platinum dish, sodium acetate is added to adjust the pH to about 5 and after heating on a water bath for 45 min the excess of EDTA is back-titrated with a Cu standard solution (solution 3) using Fluorexone as indicator and an ultraviolet lamp as the light source. In this way the volumetric equivalent for the sum of Al and

Cr is obtained. The Al is complexed (masked) with NH_4F and the liberated EDTA is similarly back-titrated, using the Cu standard solution. This titration gives the Al content while the amount of Cr is obtained from the difference.

The combined filtrates of the hydroxide precipitation are adjusted to a pH of 8 to 8.5 (final volume \cong 350 ml). To this solution 40 ml of a solution of 0.5 g diammonium diethyldithiocarbamate in 50 ml of water (this solution is adjusted to a pH of 8 to 8.5 with ammonia and ammonium chloride) are added in several portions, whereafter Ni and Mn are extracted with 200 ml of CHCl_3 (1000 ml separatory funnel). After the addition of the residual 10 ml of the carbamate solution no further precipitation should occur. The aqueous phase is washed with 20 ml portions of CHCl_3 until the CHCl_3 is colorless.

The combined CHCl_3 extracts [they are either of a green (Ni) and/or brown violet color (Mn^{III})] are shaken with a solution of mercury chloride (solution 4) whereby Mn and Ni are replaced by mercury. In order to avoid a great excess of mercury solution this is added until the CHCl_3 layer is colorless or faintly yellow. The shaking period should not be less than two hours. During this operation Ni and Mn are transferred to the aqueous phase, which is evaporated to dryness on a water bath. The residue is evaporated three times with 20 ml conc. HNO_3 followed by the same number of evaporations with equal volumes of conc. HCl. The dry residue is taken up in 80 ml of 0.1 N HCl and to this solution 1 g each of hydroxylamine hydrochloride and thiosemicarbazide are added. An excess of mercury is removed by addition of NH_3 . After standing for 2 hours on the water bath the precipitate is filtered off and the filtrate as well as the washing solution (20 ml 0.1 M NH_3) are collected in a 250 ml titration flask. After the addition of 5 ml of a buffer solution of pH 10 the sum of Mn and Ni are titrated under the ultra-violet lamp using Fluorexone as the indicator and solution 2 as the titrant. Subsequently KCN is added to liberate the amount of EDTA which is equivalent to the Ni. Then the solution is back-titrated with Mn standard solution (solution 5). The Mn is obtained from the difference.

The aqueous phase after the carbamate-chloroform extraction now contains only the ions of the alkaline earths and of the alkali metals as well as the excess of diammonium diethyldithiocarbamate. This solution is evaporated to dryness on the water bath. The residue is fumed three times with 20 ml each of conc. HNO_3 . The residue is taken up with 1 ml 6 N HNO_3 and 40 ml hot water and the solution is transferred to a 100 ml measuring flask. In an aliquot of this solution adjusted to pH 10 the sum of the alkaline earth metals is titrated with solution 2 using Eriochrome Black T as the indicator. In the residual volume of the solution Ca is precipitated with ammonium oxalate. After filtration of the calcium oxalate the filtrate contains Mg and ammonium salts as well as the ions of the alkali metals. The calcium oxalate precipitate is dissolved on the filter with hot 3 N HCl and this solution is evaporated to dryness in the presence of 10 ml of conc. HNO_3 . The residue is taken up with 20 ml of 0.1 N HNO_3 . After the addition of 10 ml 1 N NaOH the Ca is titrated with solution 2 using Fluorexone as the indicator and an ultra-violet lamp as the light source. The Mg is obtained from the difference.

Determination of silica and sulfur

200 to 300 mg of the meteorite are thoroughly mixed in a nickel crucible with an about 5-fold amount of a mixture of sodium peroxide and sodium-potassium carbonate. This mixture is carefully heated. Subsequently the temperature is gradually increased until a clear melt is obtained. After cooling,

the melt is taken up with 300 ml of water. At this stage the vessel in which this dissolution is carried out has to be covered with a watch glass (evolution of oxygen). Then the solution is evaporated to dryness with aqua regia followed by several evaporations with conc. HCl. The dry residue is taken up with water and dilute HCl, silica is filtered off and determined gravimetrically. In the filtrate sulfur is also determined gravimetrically after its precipitation as BaSO₄.

Analysis of Iron Meteorites

The analysis of the iron meteorites deviates from that of the stone meteorites with respect to the following points:

1. At least 600 mg of the sample are dissolved at a moderate temperature in a high walled beaker using 15 ml of water and 50 ml of aqua regia. The beaker is placed on a water bath until effervescence ceases. Then the solution is evaporated to dryness. The residue is fumed to dryness by using three times 20 ml of conc. HCl, and the last residue is taken up with 50 ml of hot 0.5 N HCl. Insoluble material is separated by filtration through a blue ribbon filter. The precipitate is ignited in a platinum crucible and weighed. By using a mixture of hydrofluoric and nitric acids silica is removed and the silicate content measured by determining the difference in weight. The filtrate is treated in the same way as in the case of stone meteorites.

2. Due to the fact that the Co content of iron meteorites is higher its titration is carried out using solution 2.

3. Prior to the precipitation of the hydroxides of Al and Cr, 10 ml of a 0,01 M solution of FeCl₃ are added as a collector, because these elements are present in iron meteorites in small amounts only. Before the chelatometric determination of these elements the iron is removed by ion exchange using a small column of an anion exchanger. The determination of Al and Cr using solution 1 is performed in the same manner as in the case of the stony meteorites.

4. Before precipitating Ni and Mn as the carbamates the solution is transferred to a measuring flask and 1/5 of the volume is used for the gravimetric determination of sulfur as BaSO₄.

5. Because the Ni content of the iron meteorites is higher than that of the stony meteorites the 5 fold amount of diammonium diethyldithiocarbamate is dissolved in 50 ml of water.

6. Due to the fact that the ratio of Ni to Mn is very high in iron meteorites the determination of Mn by back-titration is relatively inaccurate. Therefore in an aliquot the sum of Ni and Mn is determined. In the residual solution Ni is masked with KCN and Mn alone is titrated under the same conditions as selected for stony meteorites.

7. After the separation of Mn and Ni the whole fraction containing the alkaline earth metals is used for the determination of the sum of these elements employing solution 1. The titrated solution is evaporated to dryness, fumed three times with 20 ml each of conc. HNO₃ and in the residue the Ca is titrated as in the case of the stony meteorites.

Solutions

Solution 1. 0.005M EDTA solution.

Solution 2. 0.04 M EDTA solution.

Solution 3. 0.02 M copper sulfate solution.

Solution 4. A saturated solution of mercuric chloride is mixed with a saturated solution of ammonium tartrate of pH 8.5. A precipitate which may be formed is filtered off.

Solution 5. 0.004M manganese (II)-solution.

This working procedure was first applied to the analysis of two synthetic samples which had been prepared by the dissolution of known amounts of the various components. For this purpose high-purity metals from Fluka Co. as well as from the Unterharzer Berg- und Hüttenwerke Ges. m. b. H. (Goslar, Germany) had been used. In Table 1 the results of these investigations are shown.

Table 1

Element		Amount used (mg)	Amount recovered (mg)		
			1st Analysis	2nd Analysis	3rd Analysis
Iron	a)	2836.8	2824.6	2822.2	2824.0
	b)	762.0	758.4	758.2	761.0
Cobalt	a)	66.1	66.1	66.2	66.1
	b)	20.3	20.1	20.2	20.1
Nickel	a)	435.7	435.2	435.1	434.8
	b)	56.2	56.1	56.1	56.2
Aluminium	a)	22.4	22.3	22.4	22.4
	b)	64.1	64.0	64.1	64.0
Chromium	a)	18.9	18.9	18.9	18.8
	b)	18.9	19.0	19.0	19.0
Manganese	a)	54.2	54.2	54.2	54.2
	b)	19.4	19.4	19.4	19.4
Calcium	a)	22.1	22.1	22.1	22.1
	b)	13.3	13.3	13.3	13.3
Magnesium	a)	25.3	25.3	25.2	25.3
	b)	583.0	583.1	582.6	582.7

In Table 2 are listed the results of analyses which have been performed on meteorites.

Determination of trace elements by neutron activation analysis

Activation analysis has been applied to the determination of the following trace elements: selenium, arsenic, antimony, tin, rhenium, mercury, zinc, scandium, gold, and iridium (cobalt, chromium). For this purpose about 100 mg of each meteorite sample were irradiated together with the standards of the elements to be determined. This irradiation of the samples was carried out in fused containers of quartz. In order to avoid volatilization the mercury standard was also irradiated in a fused quartz container while the standards of the other elements were applied in closed quartz bottles.

As the source of irradiation the ASTRA-reactor of the Österr. Studiengesellschaft für Atomenergie Ges. m. b. H. at Seibersdorf with a neutron

Table 2. Component (%)

Location	SiO ₂	Fe	Ni	MgO	CaO	Cr ₂ O ₃	Al ₂ O ₃	Co	MnO	S	H ₂ O
	Stony meteorites										
Moës	38.50	22.80	1.32	25.05	1.78	0.520	2.61 ¹	0.059	0.345	2.68	0.15
Holbrook	40.73	18.49	0.97	25.62	1.88	0.477	2.81 ¹	0.060	0.510	1.98	0.34
Waconda	38.76	18.90	0.82	24.82	1.96	0.441	2.23 ¹	0.048	0.288	0.60 ³	n.d.
Knyahinya	40.70	19.26	1.01	25.79	1.62	0.470	2.44 ¹	0.058	0.440	0.43 ³	n.d.
Long Island	38.50	22.32	1.19	23.33	1.38	0.479	1.96 ¹	0.070	0.352	0.61 ³	n.d.
Sokobanja	41.82	19.07	1.02	25.46	1.90	0.395	2.44 ¹	0.059	0.370	2.04	n.d.
Stannern	44.95	14.83	≤ 0.04	5.96	10.14	0.284	12.06	5.10 ⁻⁴	0.421	trace	n.d.
	Iron meteorites										
San Cristóbal	5.58	61.59	22.53	2.49	0.39	0.061	0.235	0.603	0.340	1.19	—
Kenton County	≤ 0.05	90.32	7.21	≤ 0.05	≤ 0.05	0.058	0.026	0.456	0.022	1.13	—
Arva Magura	0.15	90.10	8.65	≤ 0.02	≤ 0.02	≤ 0.014 ²	≤ 0.02	0.550	0.059	trace	—

¹ Non-destructive activation analysis.² Neutron activation analysis.³ Sulfur found in the silicate phase.

n.d. = not determined.

flux of 10^{13} neutrons \cdot cm $^{-2}$ \cdot sec $^{-1}$ was used. The time of irradiation varied from 60 to 120 hours. After a cooling period of one day exactly weighed amounts of the meteorite samples were mixed with the corresponding carrier solutions (5 to 8 mg amounts of the elements) and

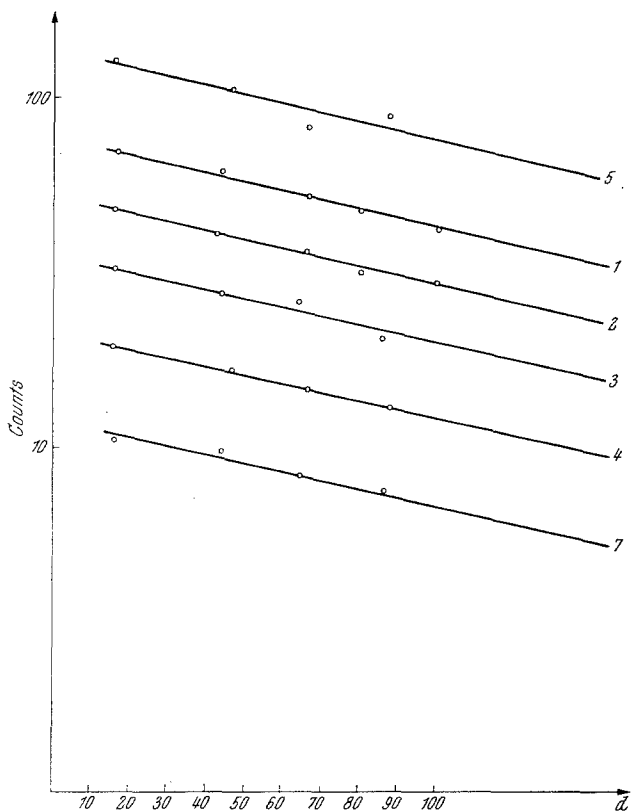


Fig. 1

transferred to a distillation apparatus made of quartz. Then the hydrogen halide distillation as described by Kiesel¹ was performed.

In addition to the elements cited by Kiesel also rhenium is volatilized under this condition, as has been shown by Geilmann et al.⁵⁻⁷. Because this element has been detected in meteorites by Goldberg and Brown⁸ it has also been included in the separation procedure and determined in the meteorites investigated by us. After the hydrogen halide distillation the

⁵ W. Geilmann und F. Weibke, Z. anorg. allgem. Chem. **199**, 120 (1931).

⁶ W. Geilmann und H. Bode, Z. anal. Chem. **133**, 177 (1951).

⁷ W. Geilmann und H. Bode, *ibid.* **130**, 323 (1949/50).

⁸ E. D. Goldberg und H. Brown, Anal. Chem. **22**, 308 (1950).

following elements to be determined were found in the distillate: selenium, arsenic, antimony, tin, mercury, and rhenium, while the residue contained

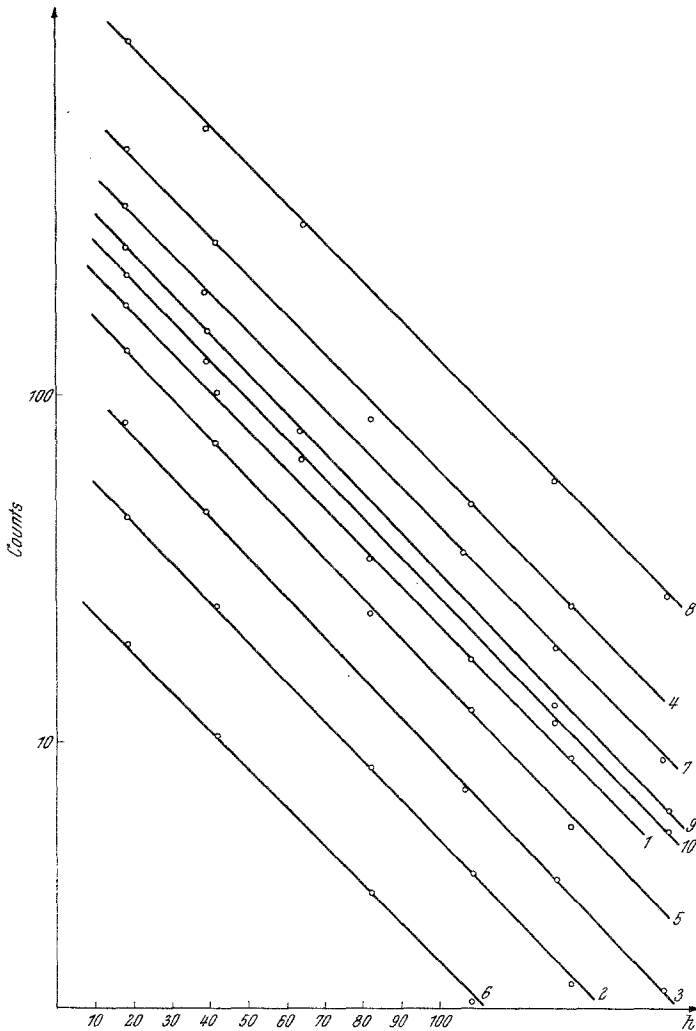


Fig. 2

among others the elements zinc, cobalt, scandium, chromium, gold, and iridium.

In the distillate the selenium was first precipitated with 7 *N* hydrochloric acid saturated with sulfur dioxide and the solution was heated for 10 min at 70–80° C on a water bath. After standing overnight the selenium was filtered off. In the presence of a foreign activity it was

necessary to reprecipitate the selenium. If this was not the case the filter was directly used for the quantitative determination. For the evaluation the 0.12 MeV photopeak of ^{75}Se was used. (In Fig. 1 the decay curves are shown.)

The filtrate which has been obtained after the precipitation of selenium was passed through an ion exchange column consisting of polyethylene (8 mm inner diameter) which had been filled with 2 g of the anion exchanger Dowex 1, X 8 equilibrated with 7 N hydrochloric acid. Under these conditions, arsenic(V) is not retained by the resin while, however, arsenic(III) and the other elements are adsorbed. To remove adsorbed arsenic(III) from the exchanger

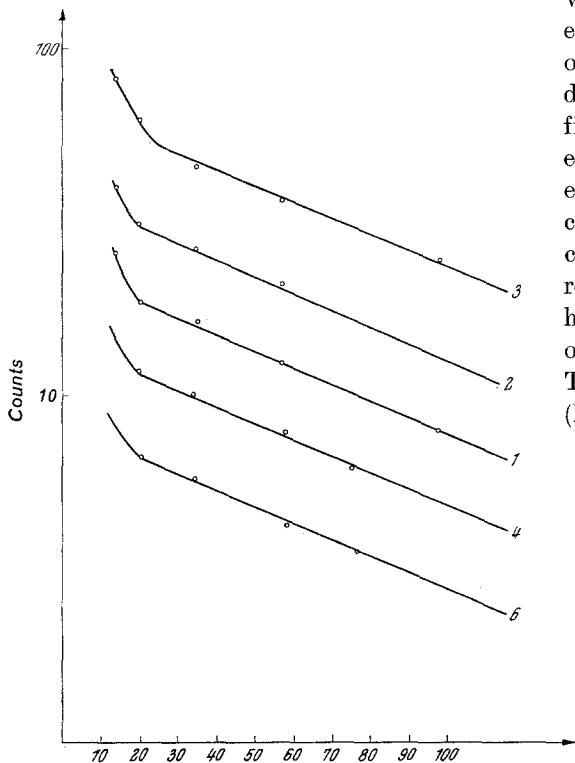


Fig. 3

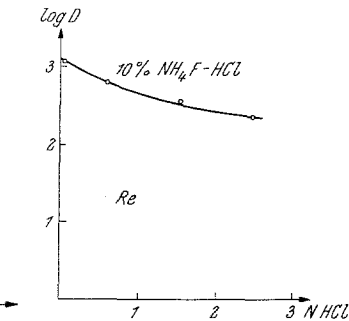


Fig. 4

this should be eluted with 3 N hydrochloric acid. Through the combined effluents hydrogen sulfide was passed, arsenic sulfide was filtered off and the content of arsenic was determined by measurement of the 0.56 MeV photo-peak of ^{76}As . In Fig. 2 the decay curves of arsenic in several meteorites, and of the standards used, are shown.

Subsequently antimony was eluted with 10% ammonium fluoride solution 0.4 N in hydrochloric acid as has earlier been described by Kiesel¹. The eluate was evaporated to dryness on a water bath and the 0.60 MeV photo-peak of ^{124}Sb was evaluated. In Fig. 3 several decay curves of ^{122}Sb (half life = 2.8 d) and ^{124}Sb (half life = 60 d) in stony meteorites are shown.

By the use of ion exchange columns consisting of plastic it was possible to subsequently elute tin with 10% ammonium fluoride 3 N in hydrochloric acid in place of employing phosphoric acid as the eluent. By these means the recovery of tin was increased to 81—84% and furthermore the time of elution was considerably reduced. Because of the fact that tin cannot readily be activated with neutrons (due to the low cross section of ^{116}Sn for thermal neutrons), only an upper limit of its concentration could be determined in virtually all cases.

Judging from the values of the distribution coefficients of rhenium on anion exchangers as given by *Kraus* and *Nelson*⁹ for hydrochloric acid solutions and from the distribution of rhenium in 10% ammonium fluoride solution at various concentrations of hydrochloric acid (see Figure 4), the rhenium is retained by the anion exchange resin by carrying out the preceding operations. This behaviour has been verified in practical runs.

In the separation procedure developed by *Kiesl*¹ the elution of tin is followed by that of mercury using 9 N nitric acid as the eluent. From the distribution ratios shown in the curves presented by *Faris* and *Buchanan*¹⁰ it is seen, however, that also rhenium is eluted at this acidity. On the other hand, it was found that the elution of rhenium is much more readily achieved so that it is possible to separate rhenium from mercury by means of ion exchange chromatography. Thus in the first 20 ml of the effluent all of the rhenium was found while mercury was only detected after 30 ml of the eluent had passed through the column. The fraction containing the rhenium was evaporated to dryness on a water bath. Its quantitative determination was performed by measuring the 0.12 MeV photo-peak of ^{186}Re . The recovery of rhenium was found to be 86 to 90%. Several decay curves are shown in Figure 5. According to *Kiesl*¹ the mercury was precipitated as copper ethylenediamine mercury iodide and determined quantitatively by measuring the 0.28 MeV photo-peak of ^{203}Hg . Under this condition, the recovery was found to be 95 to 98%. The decay curves are represented in Figure 6.

In the residue obtained after carrying out the hydrogen halide distillation only the elements chromium, cobalt, zinc, scandium, gold, and iridium have been determined quantitatively because investigations are still in progress for the isolation of other elements by means of this separation technique.

The determination of the elements mentioned above was performed in the following manner : the residue of the hydrogen halide distillation was considerably diluted with water, the solution filtered, the filter ashed

⁹ *K. A. Kraus* und *F. Nelson*, Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva 1955. Vol. 7, 113. New York: United Nations 1956.

¹⁰ *J. Faris* und *R. F. Buchanan*, Progr. in Nuclear Energy, Series IX. Anal. Chem. Vol. 6, 149, Oxford etc. Pergamon Press 1966.

and silica removed by fuming with a mixture of hydrofluoric and nitric acids. Calcium fluoride which may have been formed was brought into solution by fuming with sulfuric acid. This solution was combined with

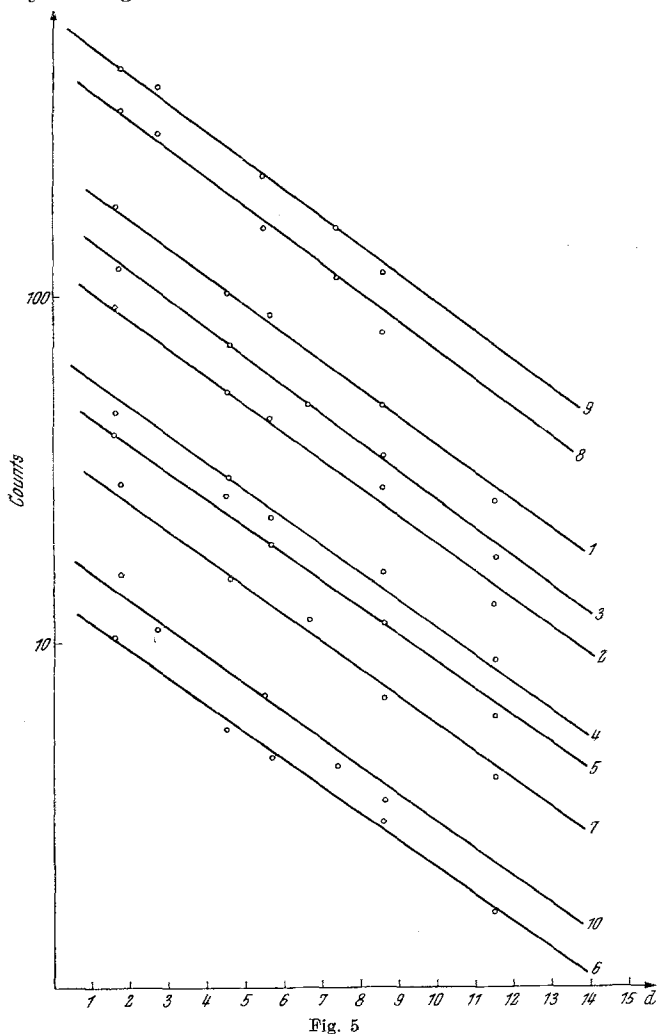


Fig. 5

the filtrate and sulfuric acid was fumed off on a sand bath. The residue was dissolved by aqua regia and several times fumed with concentrated hydrochloric acid. The last residue was dissolved in 7 *N* hydrochloric acid, carbon was filtered off and from the filtrate both iron and gold were twice extracted by diisopropyl ether.

The back-extraction of these two elements from the organic phase was performed with dilute hydrochloric acid and water for iron and gold,

respectively. The volume of the aqueous phase was considerably reduced by evaporation, the solution was acidified with hydrochloric acid and the two elements were separated on an anion exchange column of 8 mm inner diameter containing 2 g of Dowex 1, X 8. The iron was eluted with 0.5 *N* hydrochloric acid, the eluate being discarded. The elution of the adsorbed

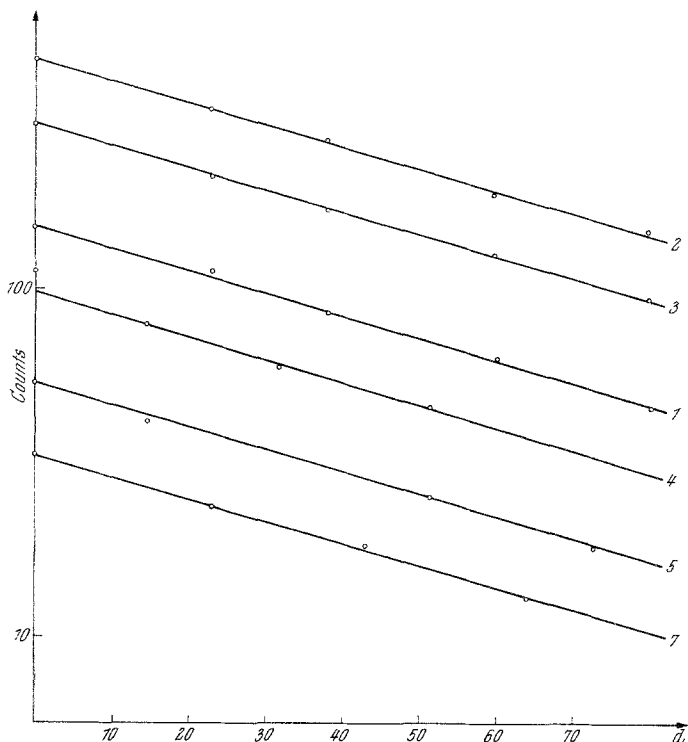


Fig. 6

auric chloride complex was performed in the same manner as the elution of the cyanide complex of gold (as described by *Burstall et al.*¹¹). The eluting agent was a mixture consisting of 5% water, 4% hydrochloric acid, and 91% acetone (the distribution ratios are shown in Figure 7).

After evaporation of the acetone the gold was precipitated with hydroquinone according to *Baedecker and Ehmman*¹². The gold was filtered off; the 0.41 MeV photo-peak of ¹⁹⁸Au was measured. The decay curves are shown in Figure 8.

¹¹ *F. H. Burstall, R. J. Forrest, N. F. Kemper und R. A. Wells*, *Ind. Engng. Chem.* **45**, 1648 (1953).

¹² *P. A. Baedecker und W. D. Ehmman*, *Geochim. Cosmochim. Acta* **29**, 329 (1956).

In Table 3 are shown the half-lives of singular nuclides which have been measured on account of the decay curves. Owing to the low activities the decay curves of long-lived nuclides have been recorded only in some cases.

The aqueous phase obtained after the extraction with ether was heated on a water bath to remove the ether and after cooling the solution was passed through an anion exchange column of 11 mm inner diameter containing 6 g of Dowex 1, X 8.

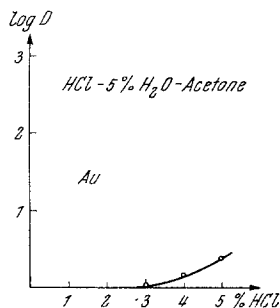


Fig. 7

The effluent containing chromium and scandium was diluted to the mark in a measuring flask. In aliquot portions of this solution chromium and scandium were determined in the presence of each other. This is possible because there is a considerable spacing between the photo-peaks of ^{15}Cr and ^{46}Sc which are at 0.32 MeV and 1.12 MeV, respectively.

Subsequently cobalt was eluted with 4 *N* hydrochloric acid and the measurement was also performed in an aliquot portion of the eluate. Finally zinc was eluted with water and determined quantitatively by measuring the 1.11 MeV photo-peak of ^{65}Zn .

Table 3

Half-lives taken from literature	Curve	Half-lives					
		^{75}Se d	^{76}As h	^{124}Sb d	^{186}Re d	^{203}Hg d	^{199}Au d
		120	26.7	60	3.80	47	2.70
Standard	1	119	26.5	63	3.80	47.0	2.75
Moës	2	121	26.5	61	3.80	48.0	2.75
Holbrook	3	122	26.0	63	3.70	47.5	2.80
Long Island	4	124	27.0	61	3.85	46.5	2.80
Sokobanya	5	117	26.0	—	3.95	46.5	2.65
Wakonda	6	—	27.0	61	3.90	—	2.65
Knyahinya	7	122	27.0	—	3.90	48.0	2.65
Arva Magura	8	—	27.0	—	3.70	—	2.70
Kenton County	9	—	26.5	—	3.70	—	2.65
San Cristóbal	10	—	26.5	—	3.85	—	2.70

To determine the iridium which was being still adsorbed on the exchanger, the resin was rinsed from the column and measured after drying. This operation is necessary because all trials to elute quantitatively the iridium from the column have failed. In some cases, however, the

Table 4. Components (ppm)

Location	Sc	As	Sb	Sn	Re	Hg	Au	Ir	Sc	Zn
Moós	10.6	1.70	0.34	≧ 2	0.033	8.80	0.135	0.72	8.56	57.1
Holbrook	8.4	2.70	3.30	≧ 2	0.032	1.80	0.200	0.35	9.70	56.0
Waconda	7.1	2.50	0.07	≧ 1	0.055	4.40	0.030	0.70	11.44	44.0
Knyahinya	11.7	0.80	0.17	≧ 1	0.041	3.80	0.120	0.22	10.20	35.2
Long Island	8.3	2.80	0.17	≧ 1	0.025	10.10	0.210	0.50	14.68	48.0
Sokobanya	5.6	1.90	0.05	≧ 1	0.022	4.70	0.230	0.10	12.66	33.6
Stannern	0.5	0.30	0.91	≧ 1	0.001	0.30	0.060	0.08	30.80	3.70
				Stony meteorites						
				Iron meteorites						
San Cristóbal	0.13	26.70	1.90	13.0	0.023	0.14	1.70	0.58	≧ 0.38	10.6
Kenton County	≧ 0.01	2.90	0.47	≧ 1	1.460	0.03	0.42	25.30	≧ 0.17	2.1
Arva Magura	≧ 0.01	16.30	0.48	≧ 1	0.156	0.13	1.15	1.36	≧ 0.24	17.3

activity was so high that only an aliquot portion of the resin could be measured. For the evaluation the 0.48 MeV photo-peak of ^{192}Ir has been used. The results of the analysis are shown in Table 4.

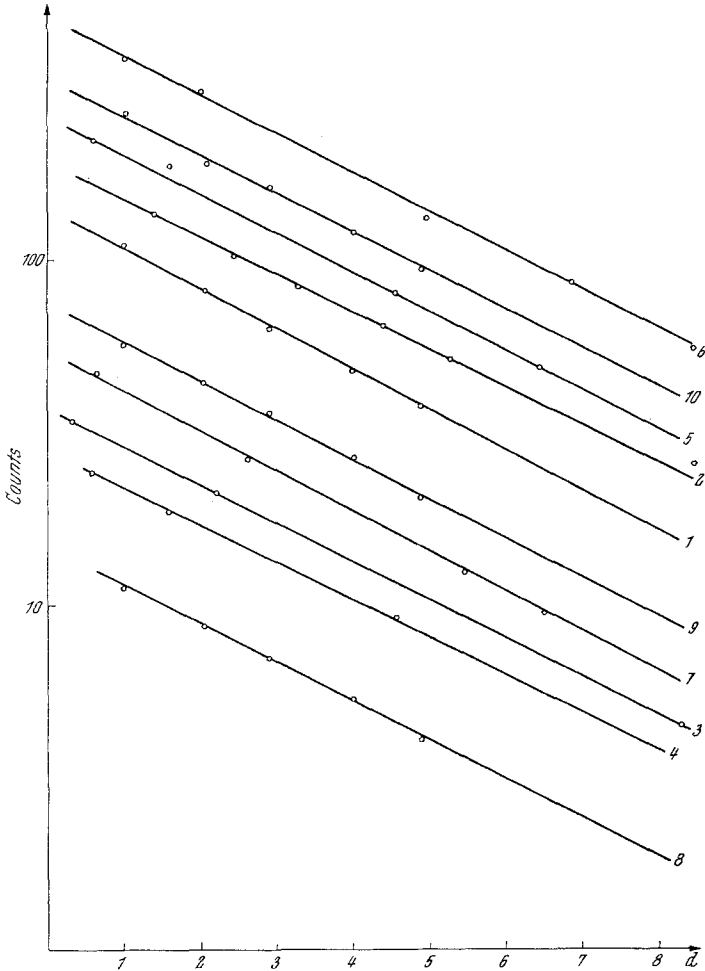


Fig. 8

Discussion

Wet-chemical analysis: A comparison with the analyses of meteorites as described by various other authors shows essentially a good accordance of results. Nevertheless one has to discuss our results with respect to several points. Because only small amounts of the meteorites Waconda,

Knyahinya and Long Island were available the value for sulfur is reliable only for the silicate-phase. Table 5 shows the sulfur content in comparison to that found by *Du Fresne*¹³ and *Mason*^{14, 15}.

Preliminary difficulties were encountered in the wet-chemical determination of aluminum. Our first data were consistently lower than those given in the literature. This was due to a defect in the method used for the dissolution of stony meteorites, whereby formation of insoluble Na_3AlF_6 was caused. Therefore this compound has to be brought into solution. Because of the small amount of sample which was available the wet-chemical analyses have not been repeated but aluminum has been determined by our collaborator Mr. *K. Leiss* using the technique of non-destructive activation-analysis.

Table 5

Meteorite	Sulfur content in %		
	<i>Du Fresne</i>	<i>Mason</i>	our values
Holbrook	2.75	—	1.98
Knyahinya	2.21	2.31	[0.43] silicate phase
Sokobanya	—	1.83	2.04

The wet-chemical values of chromium and cobalt have been checked by means of activation-analysis. As has earlier been shown by *Wood*¹⁶ the values of cobalt which are obtained by activation analysis are consistently lower than those found by wet-chemical analysis. These findings have been verified by numerous analyses of the meteorite Močs of which a larger amount was at our disposal. The values can be as much lower as about 50% in comparison to those found by wet-chemical analysis. Surprisingly in some cases, however, a good accordance was found. In the case of Holbrook the wet-chemical value for cobalt was even surpassed. A similar behavior was also observed in the case of chromium.

Insofar as conclusions can be drawn from the data available to us, the decisive factor governing this behavior is the inhomogeneity of the samples which is especially pronounced when low sample weights of about 100 mg are involved. Furthermore, sedimentation of metal grains occurs in the finest ground samples so that the analysis by activation for cobalt and chromium produces reliable results only if larger amounts of samples are used.

¹³ *A. Du Fresne*, *Geochim. Cosmochim. Acta* **20**, 141 (1960).

¹⁴ *B. Mason* und *H. B. Wick*, *American Museum Novitates* 2154 (1963).

¹⁵ *B. Mason* und *H. B. Wick*, *Geochim. Cosmochim. Acta* **28**, 533 (1964.)

¹⁶ *J. A. Wood*, *Physics and Chem. of Meteorites. The Solar System. Vol. IV.* The University of Chicago Press 1963.

In addition, the determination of sodium in meteorites according to *Schaudy*¹⁷ should be mentioned here.

For our further investigations we expect that larger amounts of meteoritic material can be made available, so that the difficulty mentioned above will be overcome and furthermore that it will be possible to determine phosphorus and potassium.

Trace Elements

Selenium. In Table 6 a comparison of the values of *Du Fresne*¹³ obtained by activation analysis and of those determined in our laboratory is made.

Table 6

Meteorite	Selenium content (ppm)	
	<i>Du Fresne</i> (l.c.)	Our values
Holbrook	13.4	8.4; 8.2; 8.5
Knyahinya	9.1	11.7

Selenium is only present in the silicate phase in which it is evenly distributed.

Arsenic. This element is enriched in the metallic phase of the meteorites. Our results correspond to the at present known abundance of these elements in meteorites. Because of the small sample size and of the pronounced inhomogeneity of San Cristóbal its content of arsenic of 26.70 ppm does not represent a mean value. This content is more nearly identical to the content of arsenic in the metallic phase.

Antimony. Attention should be paid to the high antimony content of Holbrook. If the piece analyzed by us has previously been contaminated or if it actually contains this extremely high antimony content can only be ascertained by the analysis of other fractions of this meteorite. Very probably the mean value of 3.30 does not seem to be representative because three analyses showed considerably deviating results, namely: 1.45; 6.50 and 1.95 ppm.

Tin. Except for San Cristóbal only an upper limit of the concentration was given.

Rhenium. Only the extremely high rhenium content of Kenton County is surprising.

Mercury. In this case the strongest deviations in comparison to other values given in the literature occur. *Ehmann*¹⁸ cites a mean content of ²⁰²Hg of 30 ppb, and for Holbrook 52 ppb were found. This corresponds to an overall concentration of mercury of about 0.100 to 0.150 ppm.

¹⁷ R. *Schaudy*, submitted for publication.

¹⁸ W. D. *Ehmann*, *Geochim. Cosmochim. Acta* **17**, 125 (1959).

Already *Reed et al.*¹⁹ have pointed out the possibility that this element may be volatilized during the dissolution step. When employing the distillation method described here by us, which allows the quantitative separation of volatile components without preliminary chemical treatment of the meteorite, no loss of mercury occurs. Nevertheless special attention has been paid to the determination of mercury and a series of analyses has been performed, the results of which are listed in Table 7.

Table 7

Meteorite	Mercury content (ppm)				
	Močs	8.5	10.0	8.5	6.3
Holbrook	1.8	2.3	1.2		

In fact the abundance of mercury in chondrites seems to be considerably higher than has earlier been assumed.

Gold. It should be mentioned here, that the values obtained are not absolutely representative for a mean value. This element seems to be inhomogeneously distributed in the silicate as well as in the metallic phase as is illustrated by our own inconsistent results as well as by those obtained by *Schaudy*¹⁷. For the Močs meteorite, for example, values of 0.120, 0.215 and 0.070 ppm were found in three analyses.

For olivine-hypersthene chondrites a gold content of 0.13 to 0.26 ppm is cited by *Baedecker* and *Ehmann*¹².

Iridium. Also in the case of iridium there seems to exist a strong inhomogeneous distribution among the meteorites. Analyses of *Baedecker* and *Ehmann*¹² are an example. In Table 8 some values are shown for the purpose of comparison.

Table 8

Meteorite	Iridium content (ppm)	
	<i>Baedecker</i> and <i>Ehman</i> ¹²	Our results
Long Island	0.50	0.50
Močs	—	1.20; 0.70; 0.46; 0.53
Bruderheim	0.51; 0.47; 0.40	—
Holbrook	—	0.30; 0.39
Cañon Diablo	1.5; 2.5	—

In Kenton County we have found an iridium content of 25.30 ppm which is extremely high even for iron meteorites.

¹⁹ *G. W. Reed, K. Kigoshi und A. Turkevich, Geochim. Cosmochim. Acta* **20**, 122 (1960).

Scandium. This element is only present in the silicate phase in which it is rather evenly distributed. The scandium content increases with the aluminum oxide content, although not in the same ratio as is shown by a comparison between the olivine-hypersthene-chondrites and the Stannern. *Kemp*²⁰ cites scandium contents in chondrites which vary between 7.9 and 9.7 ppm. In Table 9 some values are shown for the purpose of comparison.

Table 9

Meteorite	Scandium content (ppm)	
	<i>Greenland and Lovering</i> ²¹	Our values
Holbrook	9.2	9.75; 9.64
Močs	15.9	8.34; 8.65; 8.15; 9.10

Zinc. This element was earlier determined in meteorites by *Nishimura* and *Sandell*²². In 13 samples, values between 35 and 70 ppm were found in olivine-hypersthene chondrites. Also here the distribution in the silicate phase does not seem to be regular so that a representative mean value can only be obtained when larger amounts of samples are analyzed. In Table 10 some values are shown for the purpose of comparison.

Table 10

Meteorite	Zinc content (ppm)		
	<i>Nishimura and Sandell</i> ²²	<i>Greenland and Lovering</i> ²¹	Our values
Holbrook	42; 35	29.9	57.0; 55.0
Močs	—	58.4	59.0; 57.9; 54.3

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²⁰ *D. M. Kemp*, Anal. Chim. Acta **23**, 410 (1960).

²¹ *L. Greenland* und *J. F. Lovering*, Geochim. Cosmochim. Acta **29**, 821 (1965).

²² *M. Nishimura* und *E. B. Sandell*, Geochim. Cosmochim. Acta **28**, 1055 (1964).