

## QUANTITATIVE SEMIMICRO INORGANIC PROCEDURES

by

CHARLES L. RULES

*Dept. of Chemistry, University of Michigan, Ann Arbor (U.S.A.)*

### INTRODUCTION

The wide popularity of micro and semimicro quantitative organic procedures is undoubtedly to be attributed to their timesaving features more than to any justification based on limited availability of sample; this factor has been well discussed by HALLETT<sup>1</sup>. With respect to all typical analytical operations with the possible exception of weighing (dissolution of the sample, evaporations, filtration and washing, drying or ignition, etc.) the same favorable time comparisons would seem to apply to inorganic procedures. The approximate figures recorded in Table I emphasize this point. Reduced-scale techniques, however, have only been applied to inorganic procedures in relatively isolated instances.

TABLE I

MACRO *vs.* MICRO TIME-REQUIREMENTS FOR TYPICAL ANALYTICAL OPERATIONS

Operation	Time required, min	
	Macro	Micro
Solution or fusion	30	12
Bringing a liquid to b.p.	20 (200 ml)	2 (2 ml)
Evaporation to dryness	70	10
Filtration and washing	45	10
Drying or ignition of pp'tt.	60	15
Cooling prior to weighing	50	25
Electrodeposition	80	30

This discrepancy in practice appears to rest in large part on a rather fundamental difference between organic and inorganic analytical problems; whereas both macro and micro organic procedure tends to fall in the "unit-operations" category, "multiple-operations" involving six or more samples are conventional in inorganic practice. Accordingly, while the microchemist may well boast that his micro-drying-block will dry a precipitate in only 15 minutes

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whereas 30 to 40 minutes are required in a conventional drying oven, it is also true that six samples would require six times 15 minutes of his time against only 35 minutes with a drying oven. Nor does his salvation lie in obtaining six drying-blocks, since it would require much more than 15 minutes to place six microbeakers and filtersticks into position, adjust the temperature of each block, regulate the suction devices, etc.

The situation just noted applies as well to other operations. Thus, while a *single* "filter-paper and funnel" macro filtration is a rather slow and inefficient process, very *little additional time* is involved when a rack of *six* funnels is handled at one time. Hence the situation evidenced in Table I, which is based upon a *single* sample, no longer holds true when two or more samples are considered. Taking the time for a single-sample microdetermination as unity, a rough comparison of the time-requirements for macro *vs.* micro practice as a function of the number of samples handled is presented graphically in Fig. 1. The figures employed in devising this graph are exclusive of weighing-time and are based on typical gravimetric procedures (volumetric and electrolytic procedures show the same trends but not as markedly). In general, one may conclude that two or more samples may be handled as efficiently by macro- as by micro-scale techniques.

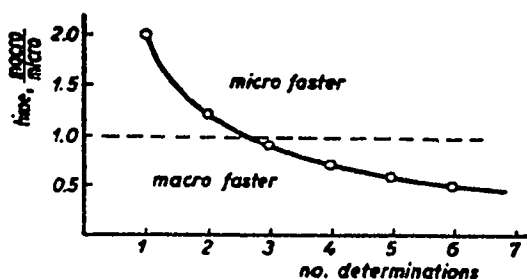


Fig. 1. Relative time required for macro *vs.* micro inorganic analyses as a function of the number of samples processed at one time. Based upon a single micro-determination as unity

Much time, unfortunately, has been devoted to devising microapparatus which will accommodate a single determination. Water baths, filter assemblies, drying devices, etc., are more often than not designed to hold a single micro beaker (see, e.g., the excellent and extensive descriptions of micro-analytical ware in p. 4 to 145 of HECHT AND DONAU<sup>2</sup>). Practical inorganic work involving six or more samples is nevertheless possible employing a semimicro scale and enjoying an appreciable saving of time over macro practice. Selected gravimetric, volumetric, and electrolytic procedures using samples of 23 to 62 mg are discussed from the standpoint of time-required and accuracy-obtained.

Experimental

#### EXPERIMENTAL

All weighings were performed on an Ainsworth keyboard type TCX semimicro balance. Weights were recorded to the nearest 0.005 mg, and the reproducibility of the balance using this practice was found to be plus or minus 0.01 mg. The "flannel and chamois" wiping technique was not employed in the case of the

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one low-temperature drying form used; its omission, however, results in only a small saving in time since its inclusion somewhat shortens the time required for cooling prior to weighing (see, e.g., p. 192 BENEDETTI-PICHLER<sup>3</sup>). Earlier experiments by the author using glass vessels of 7 to 8 grams mass and a microanalytical balance, indicate that a weight-reproducibility of between 0.008 and 0.011 mg is attainable without employing the wiping technique provided that a drying-temperature reproducibility of plus or minus 5° C is maintained. The simplification is therefore justified for most semimicro work.

Electrolyses were conducted in the CLARK AND HERMANCE cell<sup>4</sup> employing air stirring and a conventional power source. Since only two cells and two pair of electrodes were available, only two electrodepositions could be conducted at one time. This situation, however, does not differ from the custom in macro-practice except for rather special installations.

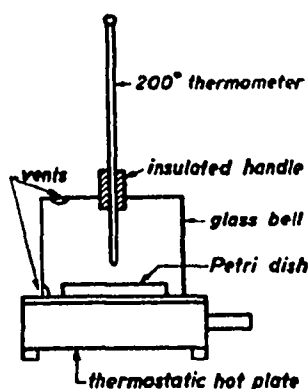


Fig. 2. Fisher Micro Dome Oven. A thermostatic hot-plate regulates the temperature of a small glass-enclosed chamber

Six or eight small vessels may be dried very conveniently in the compact hot-plate type of oven (Fisher Micro Dome Oven), consisting of a thermostatically controlled hot-plate bearing a glass shelf and larger glass cover (Fig. 2). The availability of several such devices in the laboratory will permit concurrent work with determinative forms requiring a variety of drying temperatures.

Ignitions were conducted in a small muffle furnace (Temco Model GRP) using porcelain ignition capsules to seat the crucibles. The employment of a "small" muffle has the particular virtue that the requisite temperatures are more quickly attained.

0.05000 normal potassium bichromate solution was made up and used at 25° C. Calibrated burets of 10 × 0.02 or 5 × 0.01 ml capacity were used. A silver reductor of reduced size was found convenient (Fig. 3).

For convenience, samples for the two gravimetric determinations were dispensed by gravimetric-aliquoting of a standard solution of known weight-percent composition. This could be done with sufficient accuracy by weighing to the nearest 0.5 mg on a conventional analytical balance.

#### VOLUMETRIC IRON

The direct determination of iron after reduction in 10%

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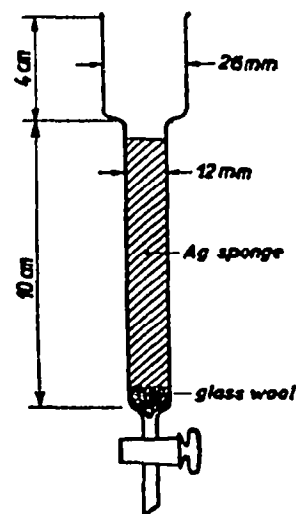


Fig. 3. Small silver reductor. Dimensioned for semimicro work with 5 to 20 ml volumes of solutions.

hydrochloric acid with the silver reductor<sup>5</sup> and using a mild oxidant such as bichromate is a particularly selective procedure. Molybdenum is the only common interference, and must be removed prior to the reduction by acid-sulfide precipitation or other means.

#### Procedure

A sample of 20 to 70 mg is weighed into a clean 8 ml platinum crucible and treated with 0.5 to 0.6 ml of conc. hydrochloric acid and 6 or 7 drops of hydrofluoric acid. The mass is warmed gently until it is reduced to *c.* 0.1 ml volume. If dissolution of the sample appears to progress satisfactorily with this treatment, 2 ml of 1:1 hydrochloric acid are added and the solution is transferred to a 30 or 50 ml beaker while washing generously and diluting finally to 10 ml volume. If the sample is incompletely attacked with acids, the mass is taken to dryness, 0.5 g of anhydrous sodium carbonate is added, and the whole fused to a clear melt. The cooled crucible is treated in a covered 100 ml beaker with 8-10 ml of hot water, adding conc. hydrochloric acid dropwise until the mass is dissolved and the alkali neutralized. The crucible is rinsed and withdrawn, 3 ml of 1:1 hydrochloric acid are added to the beaker and the volume adjusted to 15 ml. Unless the reductor contains acid from a previous pass, the following solutions are passed in order and collected in a 50 ml Erlenmeyer flask; (excess water in reductor, discarded), 5 ml of 10% HCl, the sample solution in 10% HCl, a 5 ml rinse of the sample vessel with 10% HCl, a second 5 ml rinse with 10% HCl, 5 ml additional of HCl to rinse the reductor, (10 to 15 ml of water to fill the reductor unless a succeeding determination follows immediately). Two ml of syrupy phosphoric acid and 1 drop of 0.2% sodium diphenylamine sulfonate indicator solution are added. The solution is titrated slowly with 0.05 *N* bichromate until near the end point, when an additional drop of indicator solution is added.

TABLE II  
SEMIMICRO VOLUMETRIC DETERMINATION OF IRON

Material	Sample mg	% Fe	
		Found	Theory
Argillaceous	56.34	1.14	1.14
Limestone	51.09	1.13	
(Bur. Std. No. 1a)	62.18	1.14	
Slag (52.5% SiO <sub>2</sub> , 1% Al <sub>2</sub> O <sub>3</sub> , 1.5% CaO, 4.4% MgO)	23.06	27.20	27.35
	28.24	27.52	
	25.11	27.61	
	23.78	27.46	
	24.83	27.16	
Crescent Iron Ore (Bur. Std. No. 26)	40.27	58.49	58.62
	38.86	58.65	
Sibley Iron Ore (Bur. Std. No. 27b)	33.76	67.92	68.23
	36.35	68.15	
Magnetite Iron Ore (Bur. Std. No. 29a)	35.12	69.41	69.45
	32.53	69.50	
	34.71	69.36	

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and the titration concluded. A gross blank-correction (for reagents, indicator, and reductor) of from 0.03 to 0.05 ml was always found for the conditions cited. This, of course, should be individually established and will be slightly larger when the carbonate fusion is required.

Typical results by this procedure are given in Table II. A 5 ml buret was used in the case of the first two samples. Fusion was employed in the case of the Crescent and the Sibley ores. The precision and accuracy of the technique can be seen to compare very favorably with macro practice. There is some justification for concluding that the inferior precision in the case of the sample labelled "slag" is due to poor sampling and heterogeneity (the material was ground only to 40-mesh size). Six acid-soluble samples could be processed in seventy minutes inclusive of weighings.

#### GRAVIMETRIC CHLORIDE AND ZINC

The standard gravimetric procedures of chloride as the silver salt and zinc as the pyrophosphate were selected as common and typical cases for study. Attention was focused on the time required and precision obtained in the basic "determination" only, without regard for preliminary separation techniques. Samples were taken from carefully standardized solutions of sodium chloride in 0.1% nitric acid and zinc sulfate in 1% sulfuric acid.

##### *Chloride Procedure*

A sample containing 2 to 20 mg of chloride is dispensed into a 30 or a 50 ml beaker and diluted to *c.* 20 ml volume. 0.5 *M* silver nitrate is added dropwise, while swirling the solution, until an excess of 3 or 4 drops is present. The beakers are then warmed on the hot plate to near boiling, removed, and set aside for 10 or 15 minutes with occasional stirring. The precipitate is filtered with suction through a 1.5 ml Gooch crucible (Coors No. 0) which has been tared after drying for 30 min at 150° C. The transfer of the precipitate may be accomplished either by manual pouring or by a suction-filter-siphon which connects to the crucible through a suitable one-hole rubber stopper (about the middle one-third of a No. 0 stopper). While the author agrees with the observation of INGRAM AND WATERS<sup>8</sup> that the WINTERSTEINER transfer-assembly is unreliable, the simpler modification of a siphon-tube entering the crucible through a one-hole stopper seems to give little difficulty. The last traces of precipitate are transferred and washed with 6 or 8 ml of 0.5% nitric acid (in smaller portions), employing a "feather" policeman if necessary, followed by 2 or 3 2-ml portions of 10% alcohol. Suction is continued for several minutes after the final wash. The crucibles and their contents are then dried for *c.* 30 minutes on a hot plate oven. The crucibles are cooled in an aluminum desiccator (containing no desiccant) for 10-15 min, and then on a metal cooling block alongside the balance for a further 8-10 minutes prior to weighing.

##### *Zinc Procedure*

The acidic sample solution, contained in a 50 ml beaker, is diluted to 25 ml volume, treated with 1-2 drops of methyl red indicator and neutralized by dropwise addition of 1:1 ammonia using no more than 1-2 drops excess. The beakers are transferred to a warm hot plate and the solutions treated with 10% diammonium hydrogen phosphate reagent. The reagent is added, dropwise, while stirring, to 0.2-0.3 ml excess. The suspensions are warmed for 8 or 10 min with intermittent stirring. The beakers are then placed in a shallow bath containing cool water (a

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large crystallizing dish is convenient) and the precipitates are allowed to settle. Several drops of reagent are carefully added to each determination to check for completeness of precipitation. The determinations should stand for at least 20 minutes with occasional stirring. Filter with suction through a tared (after drying at 1000°C.) 8 ml porcelain frit crucible (Royal Berlin No. 0.9974 A2). Transfer by manual pouring using 15 to 20 ml of cooled distilled water as a wash. The wash water is delivered from a graduated 50 ml micro wash bottle and the volume used is noted. Several ml of 50% ethanol are used as a final wash (a few drops may well be applied earlier as an aid in transferring the last traces of precipitate). The frits are sucked as dry as possible, removed to porcelain ignition capsules and placed in the cold muffle. The muffle is turned on for fastest heat, and the crucibles may be removed as soon as a temperature of 950-1000°C is attained (the entire process required about 25 min with the furnace used). Any deviations from this technique for adaption to other types of apparatus must allow for (a) predrying at 110-160° to avoid cracking the frits, (b) gradual increase of temperature beyond this point to prevent too vigorous an expulsion of ammonia and water, and (c) a final temperature of at least 900° should be reached. The crucibles and capsules are first cooled from red heat on an open asbestos board (Transite) for *c.* 5 min before the crucibles (alone) are distributed on the clean porcelain plate in a sizeable desiccator of conventional design (but which should contain either no desiccant or a very weak agent such as calcium chloride) for a cooling period of 15 min. The crucibles are finally placed for 10 min on a metal block before the balance before weighing. A solubility correction of 0.11 mg per 10 ml of wash water used is applied to each recorded weight of zinc pyrophosphate.

TABLE III  
SEMIMICRO GRAVIMETRIC CHLORIDE AND ZINC

Chloride as AgCl (Cl in mg)		Zinc as Zn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> (Zn in mg)		
Taken	Found	Taken	Found	
2.00	2.01 2.00	2.00 <sup>b</sup>	2.10 <sup>b</sup> 2.09 <sup>b</sup>	
5.01	5.01 5.03	5.24 <sup>b</sup>	5.25 5.25	
10.02	10.00 9.99	10.49	10.48 10.50	
20.04	20.03 20.07	20.98	20.97 21.01	
25.05	25.04 25.05	52.45	52.43 52.52	52.37 52.47

The treatment of six chloride samples required about 60 minutes, while six zinc samples were processed in about 110 minutes inclusive of the digesting and cooling periods (which time, of course, may be used in part for other work). It is felt that these times represent a considerable improvement over the comparable case in macro work. The precision and accuracy of the results obtainable leave little to be desired as is evident from the data given in Table III.

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## ELECTROLYTIC COPPER

Despite the absence of any favorable gravimetric factor, the electrodeposition of copper as the metal retains its popularity because of its simplicity, cleanliness, and rather good separation features (in a nitric acid medium). The only common interferences are fairly readily removable, silver as the chloride and tin as meta-stannic acid. The latter is no longer so tedious since the introduction by CALEY AND BURFORD<sup>7</sup> of the ammonium iodide volatilization technique, which not only gives reliable tin values but also expedites the necessary recovery of impurities for subsequent copper and lead determinations. The PREGL cell, which is prone to give low results with nitric acid media, is best replaced with the more convenient design of CLARK AND HERMANCE. The air-stirring employed with the latter has the further advantage of permitting direct copper determinations on ferrous alloys as pointed out by MACNEVIN AND BOURNIQUE<sup>8</sup>.

*Procedure*

The sample solution, which preferably contains at least 5 mg and not more than 50-60 mg of copper, is transferred to the electrolytic cell and adjusted to 8-12 ml volume. In general, the free acidity of the final volume should either correspond to 3-4% nitric acid or to a mixture of 1-2% sulfuric acid plus 2% nitric acid (sulfuric acid is desirable as the initial solvent for many corrosion-resistant alloys, or it may be introduced in freeing the solution of chlorides by fuming). For details concerning the electrolyte composition with ferrous samples, the paper of MACNEVIN AND BOURNIQUE<sup>8</sup> should be consulted. About 20 mg of urea is added and the electrodes, one of which has been tared, are introduced. Either electrode can be used as the cathode but the larger outer-electrode is preferably used whenever 40 mg or more of copper is to be plated. The bubbler tube is regulated to a reasonable rate of flow in an external vessel of water before introduction into the cell. The voltage is adjusted to *c.* 3 v. When no more copper color is evident in the solution (usually, within 10 to 15 minutes), the air-tube and cell wall are rinsed down with 0.8-1.2 ml of water. After 5 min the upper portions are again rinsed and the electrolysis is continued for another 5 min. At the end of this time the most recently wetted portion of the electrode leads is inspected for discoloration; if no copper deposition has occurred on this area, the run may be discontinued. The air-tube is carefully withdrawn (while rinsing, if the spent electrolyte is to be saved for further work). The bottom cock is opened slightly, allowing the electrolyte to drain into a convenient vessel, while washing generously from above with distilled water. As much as 40-50 ml may well be employed for washing unless the electrolyte is required for further work. In any case, the electrodes must be completely covered with pure water before the current is broken; the plated electrode is then removed at once to an external container of distilled water. The electrode is then washed in ethanol followed by ether and dried for 5 min in an oven at *c.* 90-110°C. "Flaming off" the ether or warming directly over a burner should never be resorted to. Cooling for 5 min, either suspended in air or resting on a metal cooling block, suffices. The electrode is then suspended from the central hook of the balance pan and the final weight taken after another 5 min. Brass weights make satisfactory tares; but, in view of the long-range weight-constancy of platinum ware, it is convenient to prepare a permanent tare of heavy platinum wire for each electrode used.

Duplicate determinations could be completed in approximately 40 to 50

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minutes, inclusive of weighings. The precision and accuracy for deposits weighing more than 1 mg were quite satisfactory as shown in Table IV.

TABLE IV  
SEMIMICRO ELECTROLYTIC COPPER

Material	Sample, mg	Deposit, mg	% Cu	
			Found	Theory
Cast Iron (Bur. Std. No. 51)	100.1	0.990	0.99	1.00
	108.0	1.060	0.98	
Zn Die Casting (Bur. Std. No. 94a)	55.11	0.605	1.09	1.08
	61.25	0.660	1.08	
Cast Iron (Bur. Std. No. 115)	35.62	2.295	6.46	6.44
	30.01	1.935	6.45	
K-Monel No. 1	37.88	10.77	28.41	28.47
	44.39	12.65	28.46	
K-Monel No. 2	50.41	15.01	29.78	29.82
	52.72	15.68	29.73	
Std. Cu Sol'n.	(mg of copper)		40.12 40.15	40.14
Std. Cu Sol'n.	(mg of copper)		50.21 50.16	50.19

#### SUMMARY

Representative volumetric, gravimetric, and electrolytic determinations, many on "practical" samples of alloys or minerals, have been applied on a semimicro level. The use of classical microchemical apparatus, which is usually designed to accommodate only a single sample, has been avoided as far as possible. The time-requirements for practical inorganic analyses involving two to six samples of 20 to 60 mg size are usually only two-thirds to one-quarter of the requirement for comparable macro-scale determinations. The precision and accuracy of work at the semimicro level compare favorably with that expected in conventional practice.

#### RÉSUMÉ

Plusieurs méthodes, volumétriques, gravimétriques et électrolytiques, ont été appliquées à l'échelle semimicro et pour la plupart, à des alliages ou à des minerais. L'utilisation de microappareils pour l'analyse d'un seul échantillon a été évitée autant que possible. Le temps nécessaire pour ces dosages de 2 à 6 échantillons, de 20 à 60 mg est en général réduit aux 2/3 ou au 1/4 du temps nécessaire pour les analyses ordinaires. La précision de ces méthodes est satisfaisante et comparable à celle des méthodes classiques.

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## ZUSAMMENFASSUNG

Mit verschiedenen volumetrischen, gravimetrischen und elektrolytischen Methoden wurden Semimikrobestimmungen, grösstenteils mit Proben von Legierungen oder Mineralen, ausgeführt. Die Anwendung der klassischen mikrochemischen Apparate, welche meistens für die Bestimmung einer einzigen Probe konstruiert sind, wurde so weit wie möglich vermieden. Solche Bestimmungen von 2 bis 6 Proben von je 20 bis 60 mg dauern im allgemeinen  $\frac{2}{3}$  bis  $\frac{1}{4}$  der Zeit, die für gewöhnliche Analysen benötigt wird. Die Genauigkeit dieser Methoden ist befriedigend und mit derjenigen der klassischen Methoden vergleichbar.

## REFERENCES

- <sup>1</sup> L. T. HALLETT in N. H. FURMAN *Scott's Standard Methods of Chemical Analysis*, vol. II, ed. 5, D. Van Nostrand, New York (1939) p. 2460.
- <sup>2</sup> F. HECHT AND J. DONAU, *Anorganische Mikrogewichtsanalyse*, Springer, Wien (1940).
- <sup>3</sup> A. A. BENEDETTI-PICHLER, *Microtechnique of Inorganic Analysis*, Wiley, New York (1942).
- <sup>4</sup> B. L. CLARK AND H. W. HERMANCE, *J. Am. Chem. Soc.*, 54 (1932) 877.
- <sup>5</sup> G. H. WALDEN, L. P. HAMMETT AND S. M. EDMONDS, *J. Am. Chem. Soc.*, 56 (1934) 350.
- <sup>6</sup> G. INGRAM AND W. A. WATERS in R. F. MILTON AND W. A. WATERS *Methods of Quantitative Micro-Analysis*, Arnold, London (1949).
- <sup>7</sup> E. R. CALEY AND M. G. BURFORD, *Ind. Eng. Chem., Anal. Ed.*, 8 (1936) 114.
- <sup>8</sup> W. M. MACNEVIN AND R. H. BOURNIQUE, *Ind. Eng. Chem., Anal. Ed.*, 15 (1943) 759.

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