2. Trimethylstannyl phenolate, $C_6H_5OSn(CH_3)_3$, has been prepared by the action of trimethyl tin bromide on sodium phenolate.

3. Decamethylstannobutane, $(CH_3)_{10}Sn_4$, has been prepared.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE MEASUREMENT OF THE CONDUCTANCE OF ELECTROLYTES. II. IMPROVEMENTS IN THE OSCILLATOR AND DETECTOR

BY GRINNELL JONES AND GILES M. BOLLINGER

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The new form of alternating current bridge described in the first paper of this series[1] has been used in the study of the principles of design of cells for the measurement of the conductance of solutions. Although in most respects this bridge has met our most exacting requirements, a few improvements in the accessories of the bridge have been made which it seems desirable to describe without waiting until the results on cell design can be published.

Modification of the Oscillator to Give Low Voltages.—During the work on cells it became evident that it would be advantageous to reduce the voltage used considerably below the values (2 to 5 volts) which had been used in the study of the bridge itself and in the study of resistance boxes, in order to reduce the heating effect of the current on the cells and to study polarization and the variation of resistance with voltage which has been reported by others.[2]

The vacuum tube oscillator as originally built and described in the first paper of this series contained an output coil having 140 turns and when this coil was as close as possible to the oscillating coil, gave a maximum voltage of 5.2 volts at 2280 cycles, 4.2 volts at 1090 cycles and 2.3 volts at 500 cycles, when used to measure 10,000 ohms in the bridge. When measuring lower resistances, the voltage was somewhat less. The voltage could be diminished continuously down to about 0.2 volt by moving the output coil along its axis away from the oscillating coil to a distance of six inches, thus diminishing the inductive coupling. To reduce the voltage still more by moving the coil still farther away from the controlling coil did not seem to be wise because this would reduce the influence of the controlling coil without at the same time reducing the influence of outside disturbing factors such as electric light circuits and nearby electric motors. An attempt to reduce the voltage by the use of

[1] Grinnell Jones and R. C. Josephs, THIS JOURNAL, **50**, 1049 (1928).

[2] W. A. Taylor and S. F. Acree, *ibid.*, **38**, 2416 (1916); C. A. Kraus and H. C. Parker, *ibid.*, **44**, 2438 (1922).

taps on the output coil proved to be unsatisfactory and was abandoned. When a tap is used, the unused turns in the coil are thus appended in an unsymmetrical manner to one end of the effective part of the output coil. The unbalanced capacitance between this appended portion and the grounded shield makes it difficult to make a proper ground balance. We, therefore, built two additional output coils, one of 36 turns and one of 12 turns, each shielded by a grounded toroidal coil as described in the first paper, and mounted so as to be movable on their common axis, making it possible to vary the closeness of the coupling with the oscillating coil. The coils not in use are completely disconnected from the circuit. As thus modified our oscillator can be adjusted so as to give any desired voltage from the maximum stated above down to 0.01 volt. Above 0.3 volt these voltages can be measured by means of a thermal voltmeter. Below 0.3 volt the voltages can be estimated with sufficient accuracy for our purposes from the position of the output coil with reference to the oscillating coil. Additional condensers of smaller capacitance than those originally provided were added to the oscillator so that by their use the frequency could be adjusted up to 5000 cycles.

We found that when using very low voltages across the bridge the sensitiveness was no longer adequate for our purpose. When measuring 1000 ohms with 4 volts, the setting of the bridge could be definitely determined to within 0.001 ohm or to one part in a million, but when the voltage was below 0.4 volt it was no longer possible to maintain a sensitiveness of 0.001%, which is the precision we desired. The best remedy seemed to be an improvement in the amplifier.

Improvements in the Amplifier.—The transformers in our two-stage amplifier, which had a step-up turns ratio of 3.5:1, were built by the General Radio Company for use in radio receiving sets and were the best commercially available at the time the bridge was originally built. Recent advances in the science of radio indicated that a substantial improvement in the performance of our amplifier could be obtained by replacing these old transformers by others of superior design.

It has been pointed out by Lord Rayleigh[3] that the telephone to be used as a detector in an alternating current bridge will have the maximum sensitiveness if it is designed so that the impedance of the telephone equals the impedance of the bridge. It is an obvious extension of this principle that when an amplifier is used between the bridge and telephone it is an advantage to have the impedance of the primary in the transformer of the amplifier match the impedance of the bridge and to have the impedance of the secondary of the transformer match the impedance of the vacuum tube which serves as its load. Since the impedance of the bridge varies with the resistance being measured and the impedance

[3] Lord Rayleigh, *Proc. Roy. Soc. London*, **49**, 203 (1891).

of the primary in the transformer with a fixed inductance varies with the frequency being used, the ideal transformer would have a primary inductance which is adjustable to the most suitable value for every measurement, and a secondary which is adjustable to maintain the best step-up turns ratio.

But there are other considerations in the design or selection of transformers for this purpose. The closer the coupling between the primary and secondary, the more nearly will the effective amplification factor equal the ratio of the number of turns of winding in the secondary to that in the primary. It is also desirable to have a high step-up turns ratio, but if the turns ratio is made too great, the effective amplification factor in the transformer becomes greatly dependent on the frequency, having a sharp maximum at the natural frequency of oscillation of the secondary as determined by the inductance and distributed capacitance of the secondary and its load. The greater the resistance being measured, the sharper is the maximum of the effective amplification at the natural frequency of the oscillation of the secondary.

In the design of transformers for audio frequency amplifiers in radio receiving sets it is important that the amplification factor be as nearly as possible independent of the frequency throughout the audio frequency range to avoid distortion of music. This requirement limits the step-up ratio that can be used for this purpose. To avoid distortion, it is desirable to have the coupling between the primary and secondary as nearly perfect as possible. In recent years iron of higher permeability has become available for the core of transformers, which improves the coupling so that the step-up ratio can be increased to 6:1 without distortion, whereas a step-up ratio of 3.5 was the maximum that could be used without distortion until the better iron became available. Since we never use more than one frequency at a time it is not essential for our purposes that the effective amplification factor should be independent of the frequency and, therefore, it is possible to use greater step-up ratios.

It did not seem practicable to build a transformer which would have a primary adjustable to the most suitable inductance for each measurement and a secondary adjustable to maintain the most suitable step-up ratio and at the same time maintain a close coupling between the primary and secondary. Nor could we find available by purchase any audio frequency transformers with as low a primary inductance and as high a step-up ratio as was shown by some preliminary experiments to be desirable for our purpose. However, this difficulty was overcome through the kindness of Mr. Melville Eastham of the General Radio Company, who gave orders to have one of their standard transformers modified at the factory to serve our needs. Their transformer, Type 284,S24, which has 15,500 turns in the secondary, was modified by bringing out a tap on the primary at 400 turns (Tap I), and a tap at 1000 turns (Tap II) in addition to the original full primary winding of 2500 turns (Tap III), thus making available primary inductances of 0.3, 1.8 and 12.0 henrys, and turns ratios of 39:1 and 15.5:1 and 6.2:1, according to the tap used. In this way some adjustability is secured.

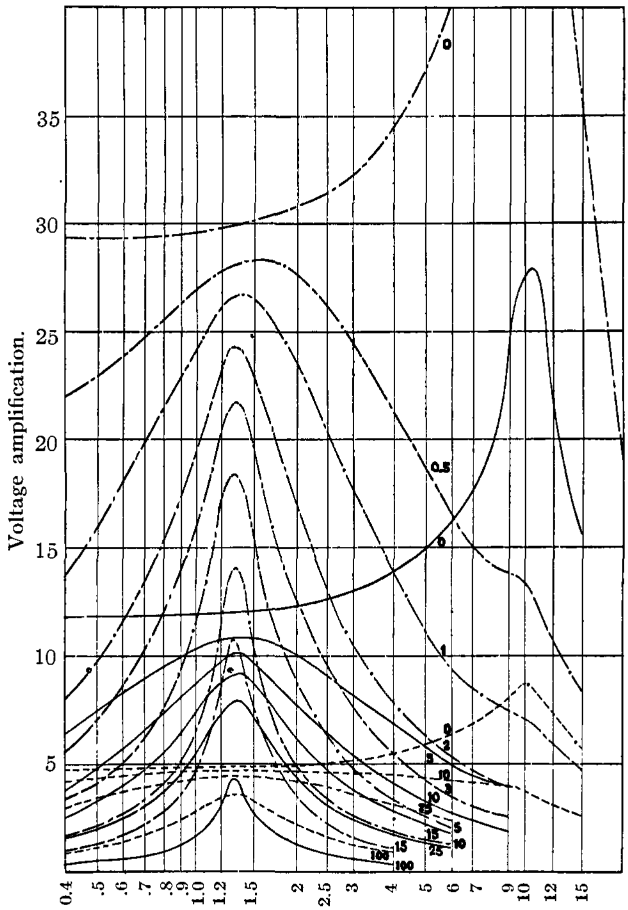
Then, through the kindness of Professor R. F. Field, who made available to us the facilities of the Cruft Laboratory and aided us by helpful suggestions, we were able to determine the actual effective amplification factor of our new modified transformer at 20 different frequencies covering the range 400 to 20,000 cycles and with various resistances covering the range 0 to 100,000 ohms in series with the primary of the transformer, using each of the three taps on the primary winding. These data are not published in full because they are applicable only to a particular instrument and are, therefore, not of general interest, but are shown graphically in Fig. 1. Extracts from these data are given in Table I to illustrate the advantages which can be gained by having a transformer which is well designed for the purpose and has taps giving some adjustability. The first column gives the resistance being measured in the bridge, R; the second column gives the corresponding effective resistance in series with the primary of the transformer, which is $(1000 + R)/2$ in our bridge with fixed ratio arms of 1000 ohms each. The body of the table gives the corresponding effective amplification factor (electromotive force at the terminals of the secondary divided by the electromotive force applied across the resistance given in the second column and the primary in series) as determined at the frequencies shown and with the taps indicated in the heading. Under the I in the heading are given the data obtained when using the first tap with 400 turns in the primary and a turns ratio of 39:1, and an inductance of 0.3 henrys; under II are the data obtained when using the second tap with 1000 turns and a turns ratio of 15.5:1 and an inductance of 1.8 henrys, and under III are the data with 2500 turns in the primary and a turns ratio of 6.2:1 and an inductance of 12.0 henrys. The figures given in parentheses are obtained by interpolation from

TABLE I

AMPLIFICATION FACTOR OF TRANSFORMER

R	$\frac{1000 + R}{2}$	500 cycles			1200 cycles			2500 cycles			5000 cycles		
		I	II	III	I	II	III	I	II	III	I	II	III
	0	*29.4*	11.9	4.8	*29.9*	12.0	4.8	*31.3*	12.6	5.0	*37.6*	15.3	5.9
0	500	*22.4*	(11.0)	(4.8)	*27.9*	(11.9)	(4.8)	*26.2*	(12.2)	(5.0)	*19.1*	(12.0)	(5.9)
1000	1000	*15.8*	(10.5)	(4.8)	*26.1*	(11.7)	(4.7)	*20.4*	(11.9)	(5.0)	*11.6*	(10.5)	(5.8)
3000	2000	*9.7*	(9.6)	(4.7)	*23.2*	(11.4)	(4.7)	*13.3*	(11.0)	(5.0)	6.3	(*8.7*)	(5.7)
5000	3000	6.6	(*8.7*)	(4.7)	*20.2*	(11.2)	(4.7)	9.5	(*10.3*)	(4.9)	4.3	(*7.4*)	(5.6)
7000	4000	5.2	(*8.0*)	(4.6)	*18.6*	(11.0)	(4.7)	7.4	(*9.7*)	(4.9)	3.3	(*6.5*)	(5.5)
9000	5000	4.1	*7.5*	4.6	*17.0*	10.7	4.7	6.1	*9.1*	4.8	2.6	*5.9*	5.3
19,000	10,000	2.0	*4.8*	4.3	*10.6*	9.7	4.6	3.2	*6.3*	4.7	1.5	3.3	*4.5*
29,000	15,000	1.3	3.3	*4.0*	8.7	*8.8*	4.6	2.2	*4.7*	4.4		2.2	*3.8*
49,000	25,000	0.8	2.0	*3.4*	5.8	*7.5*	4.4	1.3	3.1	*4.0*		1.4	*2.8*
199,000	100,000	0.2	0.5	*1.1*	1.6	3.1	*3.4*		0.8	*1.7*			

curves. The tap which should be chosen at any given resistance and frequency is shown by italicizing the highest amplification. The great improvement over the original transformer, which had a turns ratio of only 3.5 to 1, and the advantage of having several taps are quite apparent



Frequency in kilocycles, logarithmic scale.

– – – –, Tap I; ————, Tap II; - - - - - - -, Tap III.

The numbers in the figure indicate the resistance in kilohms placed in series with the primary winding.

Fig. 1.—Voltage amplification of special transformer.

from this table and the curves of Fig. 1. Thus, for example, when measuring 1000 ohms at 1200 cycles, the lower tap (I) gives an amplification factor of 26.1, which is more than five times the amplification factor of 4.7 given by Tap III, whereas when measuring 19,000 ohms at 5000 cycles, Tap III gives an amplification factor three times as great as Tap I. In the curves drawn from the complete data (Fig. 1) the natural frequency of the secondary is indicated by the maxima appearing at 1300 cycles.[4]

The selection of the most suitable tap depends both on the frequency being used and on the resistance being measured and cannot be stated in any simple manner; it can be inferred from the curves. Thus, for example, inspection of Fig. 1 shows that the curves for Tap I and for Tap II with 5000 ohms in series (which is the effective value when the resistance being measured in our bridge is 9000 ohms) cross each other at 920 cycles and again at 1800 cycles, which means that the two taps give equal amplification factors (of about 10 at 920 cycles and about 11 at 1800 cycles) with 9000 ohms in the bridge, whereas when using frequencies within this range Tap I is superior, and when using frequencies less than 920 or greater than 1800, Tap II gives the higher amplification factor.

In general, Tap I is to be preferred when measuring low resistances (3000 ohms or below) with any frequency between 500 and 3000 cycles, and can be used to advantage even when measuring high resistances if the frequency is near the natural oscillation frequency of 1300 cycles. Tap III is not to be preferred when measuring any resistance below 9000 at any frequency below 5000. When measuring high resistances, the choice between the three taps depends on the frequency. Thus, for example, when measuring 19,000 ohms in the bridge (equivalent to 10,000 ohms in series with the transformer), Tap III is best below 450 cycles, Tap II between 450 and 1150 cycles; Tap I is best in the range 1150 to 1550 cycles, which is near the natural oscillation frequency of 1300; Tap II again becomes the best in the range 1550 to 3500 and Tap III at all frequencies above 3500 cycles. It is possible to build a transformer so that it will have its natural oscillation at any frequency that may be desired.

By employing a primary winding with still fewer turns and hence a higher turns ratio than is given by Tap I—say, for example, 200 turns and a turns ratio of 78—a correspondingly greater amplification would be obtained at 1300 cycles, but calculations indicate that the curves would drop so sharply on either side of this optimum frequency when the primary was placed in series with a resistance greater than 500 ohms (the lowest limit in our bridge with fixed ratio arms of 1000 ohms each) that the advantage of a gain in the amplification factor would be offset by the narrowness of the range of frequencies over which it would be apparent.

The old transformer, originally used between the first and second stages of the amplifier was replaced by a new transformer, General Radio Type 285H, which was not on the market when the amplifier was originally built. This was an improvement because the step-up ratio was 6:1 instead of 3.5:1 and because the quality of iron is better than that in the old transformer.

The effect of these improvements was an increase of at least ten-fold in the sensitiveness of the bridge when measuring 1000 ohms with 1090 cycles and about three-fold

[4] With little or no additional series resistance in the primary circuit a maximum appears for each tap at about 10,000 cycles. The frequency at which this maximum occurs is determined by the natural frequency of the secondary and the coefficient of coupling of the transformer. The maximum voltage rise at this point depends upon the losses in the transformer and is also greatly reduced by any resistance in series with the primary. The greatest amplification factor which we found with our transformer was nearly twice the turns ratio. In the case of Tap I the amplification factor rose to a maximum value of 70 (not shown in the figure). The high increase in amplification at this point is not available for practical use because it occurs at the extreme limit of the audible range and because it disappears as soon as any appreciable resistance is placed in the primary circuit.

when measuring 30,000 ohms. The effective amplification factor of our two-stage amplifier with these improvements varies greatly with the resistance being measured and the frequency being used, but may be estimated to be of the order of magnitude of 10^3 to 10^4.

The Use of a Wave Filter.—These changes in the amplifier brought in their train two disadvantages which were especially evident when working with low voltages. The increased efficiency of the amplifier not only magnified the desired signal but also magnified all of the disturbances, such as the so-called "tube noises," sixty-cycle hum from the electric light circuit, sparks at the commutators of motors, and at the relay control of thermostat heater, all of which were audible in the telephones. The main signal was weakened by lowering the voltage of the oscillator without any corresponding weakening of these noises, so that they became more disturbing. Fortunately the remedy was easy by using so-called wave filters. By placing a variable inductor and a variable condenser both in parallel with the telephone and then adjusting the inductance and capacitance until the relation $LC\omega^2 = 1$ is satisfied, the disturbing noises are greatly reduced with very little weakening of the desired signal in the telephone. The variable inductor was a special instrument made for us by the General Radio Company. It consisted of a coil of 2800 turns of No. 28 enamel-covered wire and a sliding E-shaped laminated iron core. The center tongue could be inserted inside the coil and the outer tongues came close to the coil on the outside. By varying the position of the core with reference to the coil, the inductance could be varied from 0.12 to 1.7 henrys. The sliding core was provided with a pointer and a calibrated scale. For a variable condenser we used a General Radio decade box with dial switches giving capacitances from 0.01 to 1.0 microfarad. With the inductor set at 0.225 henry, capacitances of 0.5 μf, 0.1 μf and 0.02 μf are suitable for 500, 1090 and 2280 cycles, respectively.

Errors at Low Voltage Due to Mutual Inductance.—The other difficulty which followed the improvement in the amplifier was the observation that when using low voltage across the bridge, the setting of the bridge at balance could be varied by merely reversing the lead wires from the amplifier to the midpoint of the bridge. We had tried this experiment on several occasions in the past without finding the effect but these experiments had been made with comparatively high voltages. We now found by experiment that with the oscillator placed about five feet from the bridge the percentage effect of reversing the amplifier lead wires (1) decreased as the voltage across the bridge was increased and became negligible (*i. e.*, less than 0.001%) when 4 volts were applied at the ends of the bridge; (2) increased with the resistance being measured in the bridge; (3) was greatest when the tap at 400 turns on the primary in the first transformer of the amplifier was in use, and least when the full

2500 primary turns were used; (4) decreased with increase in frequency; (5) could be varied by rotating the oscillator on a vertical axis and a position of minimum effect could be found; (6) could be varied by rotating the amplifier and telephones. At its worst, the effect of reversing the amplifier leads was a change of 0.45% in the bridge setting. Moreover, it was noticed that a feeble note could be heard in the telephones when the amplifier was entirely disconnected from the bridge if the oscillator was operating.[5] The note was more intense when the wave filter was connected to the telephone than when it was removed. This note was at the frequency of the oscillator and stopped when the oscillator stopped and, therefore, must have been due to a direct transfer of energy from the oscillator to the coils in the transformers of the amplifier and to the coils in the telephone and wave filter through their mutual inductance.[6] That meant that as a result of this mutual inductance between oscillator and detector there was an induced alternating electromotive force at the ends of the lead wires from the amplifier. If the bridge were at true balance so that the potential between the midpoints was exactly zero and then the lead wires were connected to the bridge, a note would be heard in the telephone, and in order to get silence in the telephone, the bridge setting would have to be changed sufficiently to give a potential between the midpoints equal in magnitude and opposite in phase to the potential induced in the amplifier. On reversing the lead wires, the bridge setting would have to be changed in the opposite direction from its true setting in order to obtain a silence in the telephones. The difference in bridge setting before and after reversing the lead wires is thus twice the error caused by the mutual inductance between oscillator and detector and the average setting would be correct. The induced electromotive force at the end of the amplifier lead wires is independent of the voltage applied to the bridge because it depends upon the variable magnetic field of the oscillating coil and is not appreciably influenced by the choice or position of the output coil. The induced electromotive force at the end of the amplifier lead wires is so small that when 4 volts is applied across the bridge it has a negligible effect, but can become appreciable as the applied voltage is lowered.

Fortunately there is a simple and effective remedy for this error by moving the oscillator to a considerable distance. When the oscillator was moved to a distance of 35 feet from the bridge, the effect of reversing

[5] J. L. R. Morgan and O. M. Lammert, This Journal, **48**, 1231–1232 (1926), have observed a similar effect when using a Vreeland oscillator and have suggested the proper remedy of moving it to a safe distance. They say nothing about the variation of this error with the voltage used and do not suggest the use of an oscillator with a lower external field than the Vreeland oscillator.

[6] The oscillator was enclosed in a grounded metallic box and, therefore, the effect could not have been due to a variable electrostatic field.

the lead wires disappeared entirely and no note could be heard in the telephones when the amplifier was disconnected from the bridge.

Having found that the influence of the variable magnetic field of the oscillator on the detector became significant when using low voltages, it was necessary to reëxamine the possibility of error due to the effect of this field on the bridge itself at the lower voltages. This was tested by changing the lead wires from the resistance box to the rest of the bridge, by reversing the lead wires from the oscillator to the bridge and by moving the oscillator. Thus, for example, measuring 30,000 ohms with 4 volts and 1090 cycles with the oscillator at a distance of five feet from the bridge, the error due to mutual inductance between the oscillator and the bridge itself was only 0.0003%. This error is negligible and, together with other similar experiments not reported in detail, confirms the conclusions drawn in the earlier work with this bridge at relatively high voltages. When the voltage was reduced to 0.01 volt without changing any of the other conditions given above, the error was 0.3%. Numerous other experiments were made to determine the influence of frequency, resistance being measured and type of resistance box, but these experiments need not be discussed in detail since the removal of the oscillator to a safe distance is a complete and perfect remedy.

If the available room does not permit moving the oscillator to a safe distance, reliable results can be obtained by taking the mean of the four readings obtained by reversing the lead wires from both the amplifier and the oscillator to the bridge. This is analogous to the usual practice of eliminating error due to thermoelectric effects in direct current measurements by means of reversing switches. Effective magnetic shielding of the oscillator is so difficult as to be hardly practicable, but the oscillator may be improved so as to reduce its outside electromagnetic field.

Grateful acknowledgment is made for an appropriation from the Milton Fund for the expenses of this research.

Summary

1. When measuring the conductance of solutions it is desirable to use a low voltage in the bridge. A modification of the oscillator to give low and controllable voltages is described.

2. The use of low voltages in the bridge diminishes the sensitiveness. The best remedy is to improve the amplifier. The principles of design of the transformer for a vacuum-tube amplifier are discussed and means of increasing the sensitiveness described.

3. The use of a wave filter in parallel with the telephone is recommended.

4. The mutual inductance between the oscillator and detector and between oscillator and bridge may cause an error in the measurement

of the conductance of solutions when low voltages are being used and means for the discovery and elimination of this error are explained.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE PREPARATION OF ANTIMONY-FREE ARSENIOUS OXIDE AND THE ESTIMATION OF MINUTE AMOUNTS OF ANTIMONY IN ARSENIOUS OXIDE

BY C. W. FOULK AND P. G. HORTON

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In the preparation of arsenious oxide of a high degree of purity, antimonous oxide is, by far, the most troublesome of the impurities to remove. Chapin[1] seems to be the first to call attention to the importance of this impurity and has given a method for removing it. He points out that it is impossible to accomplish this by the usual methods of purification such as recrystallization and sublimation; indeed, he states that it is entirely possible after recrystallization and sublimation to end with a "purified" arsenious oxide more impure than the original material. On the other hand a number of careful workers have regarded these methods as sufficient. Washburn,[2] in his investigation of the theory and practice of the iodimetric determination of arsenic acid, purified arsenious oxide by recrystallization from hot water and by sublimation. Baxter and Coffin[3] in their work on the revision of the atomic weight of arsenic say, "commercial C. P. arsenious oxide was recrystallized three times from dilute hydrochloric acid solution and after being rinsed with water and centrifugally drained, it was converted into arsenic acid by means of nitric and hydrochloric acid in a porcelain dish," and "arsenious oxide was twice resublimed in a current of dry air and then once recrystallized from dilute hydrochloric acid solution."

In the present investigation Chapin's work was repeated and his method found to be all he claimed for it, but inadequate if the product is to be used in atomic weight determinations or other precise work. The following proposed method is shorter and is believed to effect not only the complete removal of antimony but to a very large extent that of all other impurities as well.

Briefly stated the new method consists in converting arsenious oxide into arsenious chloride which is then repeatedly shaken out in a separatory funnel with concentrated hydrochloric acid to remove antimony. The arsenious chloride is next hydrolyzed with water to give arsenious oxide

[1] Chapin, *J. Ind. Eng. Chem.*, **10**, 522–524 (1918).

[2] Washburn, THIS JOURNAL, **30**, 31–46 (1908).

[3] Baxter and Coffin, *ibid.*, **31**, 297 (1909).