

The Determination of Metals in Wool by Atomic-absorption Spectroscopy*

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Atomic absorption has been shown to provide a simple and precise method for the determination of chromium, copper, mercury, tin, zinc, calcium, strontium and barium in wool. The method of standard additions is used for calcium and a calibration-graph method for the other metals. Both methods have an accuracy and reproducibility of about ± 3 per cent. The wool sample is hydrolysed in constant-boiling hydrochloric acid, and the calibration graphs are prepared by using wool hydrolysates containing standard amounts of metal to compensate for physical and chemical interferences caused by hydrochloric acid, amino-acids and ions present in the wool.

THE wide use of metal salts in the treatment of wool has led to a need for rapid and precise methods for the determination of metals in wool. Recently, aluminium in wool has been determined by atomic-absorption spectroscopy.¹ Because that work showed that the method offered advantages in speed, convenience and specificity over existing methods,² the present study was undertaken with a view to analysing wool for chromium, copper, mercury, tin, zinc, calcium, strontium and barium by atomic-absorption spectroscopy.

In our previous work, the wool sample was hydrolysed by heating it overnight with constant-boiling hydrochloric acid in a sealed tube at 110° C, and the hydrolysate aspirated directly into the flame of the atomic-absorption spectrophotometer. It was possible to compensate simultaneously for both physical and chemical interferences by using solutions of wool hydrolysates to prepare calibration graphs. This technique necessarily required the wool to be free from metal ions, and for all of the metals, except calcium, this condition was obtained by repeated extraction with an aqueous 0.5 M EDTA solution. With calcium, although extraction with 0.5 M EDTA solution initially removed a considerable proportion of calcium ions, a small constant amount remained after repeated extraction. The method of standard additions³ was, therefore, used for this metal.

EXPERIMENTAL

APPARATUS—

The apparatus described previously¹ was used. Because of the relatively large size of the sample (about 0.3 g), advantage was rarely taken of the very high sensitivity possible with atomic-absorption spectroscopy and, for all of the metals, except tin and barium, a reduction in sensitivity was necessary. This was achieved either by using a less sensitive line than that normally used or by rotating the burner.⁴ This technique was preferred to dilution because it is quicker, although for zinc and strontium a dilution technique was necessary because rotating the burner did not reduce the sensitivity sufficiently, and other resonance lines of suitable sensitivity were not available. The operating conditions, shown in Table I, are not, therefore, necessarily the most sensitive, but those found to give the best results for the samples under test.

REAGENTS—

All of the reagents used were of analytical-reagent grade. Stock solutions (about 0.1 M) were prepared by standard methods.⁵ The wool used for the calibration graphs was prepared by shaking scoured wool (30 g) gently for 3 days with 800 ml of EDTA (disodium salt) solution (0.5 M). After rinsing it thoroughly in de-ionised water, the extraction with EDTA solution was repeated once more. The absence of the metal under test was confirmed by wet ashing,² freeze-drying to concentrate the sample and subsequent analysis.

* The work reported here is part of that presented to the 6th Australian Spectroscopy Conference, Brisbane, August, 1967.

TABLE I
INSTRUMENTAL CONDITIONS FOR THE DETERMINATION OF METALS IN WOOL

Element	Fuel - oxidant	Lamp current, mA	Slit width, μ	Wave-length, \AA	Burner length, cm	Burner rotation,	Approximate sensitivity*
Chromium	Acetylene - air†	10	100	{ 3578.7 4254.3 4289.7	5 5 5	40° 10° 0°	7.5 10.9 5.7
Copper	Coal gas - air	6	50	2942.1	10	0°	2.9
Mercury	Coal gas - air	4	20	2536.5	10	10°	46
Tin	Hydrogen - air	5	50	2354.8	10	0°	4.2‡
Zinc	Coal gas - air	8	300	2138.6	10	0°	0.015
Calcium	Acetylene - nitrous oxide (10:1)§	10	25	4226.7	5	0°	0.055
Strontium	Acetylene - nitrous oxide (4:1)§	10	100	4607.3	5	0°	0.20
Barium	Acetylene - nitrous oxide (2:1)†§	10	50	5535.6	5	0°	3.8

* Sensitivity is the number of milligrams of element per litre of water necessary to give 1 per cent. absorbance.

† An oxidising flame was used to reduce the background noise observed with the more sensitive reducing flame.

‡ Water contained hydrochloric acid (0.01 N) to prevent hydrolysis of tin(II) chloride.

§ Ratio of height of red "feather" to height of inner blue cone.

ANALYSIS OF SAMPLES—

Calibration-graph method—Prepare the samples and standards by hydrolysis in constant-boiling hydrochloric acid, as described previously.¹

Method of standard additions—Hydrolyse the sample, as before,¹ and withdraw, by pipette, three 1-ml samples from the hydrolysate. Dilute one of the samples to the volume necessary to give a transmittance of 80 per cent. To the others add different, but accurately known, amounts of calcium ion (about 0.6 and 1.2 p.p.m.) before making up the volume with constant-boiling hydrochloric acid. Aspirate the three samples consecutively into the atomic-absorption spectrophotometer, measure the absorbance values and repeat the readings twice more to eliminate the effect of fluctuations in the flame or instrument conditions. Determine the magnitude of the background absorbance by measuring the absorbance of the nearby 4201 \AA line that is not absorbed by calcium. The concentration of calcium in the hydrolysate can be calculated⁶ from the three corrected absorbance readings in two independent ways.

RESULTS AND DISCUSSION

SAMPLE SIZE—

It was found that if the wool samples were too small sampling errors were introduced, probably because the uptake of metal ions was not completely uniform among the fibres.

TABLE II
REPRODUCIBILITIES AND CONCENTRATION RANGES OF THE ANALYSES FOR
METAL IONS IN WOOL

Metal	Reproducibility, per cent.	Typical concentration range,* mg of metal per g of dry wool	Minimum possible concentration,† mg of metal per g of dry wool
Chromium ..	±3.4	0.7 ₈ to 29	0.03
Copper ..	±2.3	0.4 to 8	0.09
Mercury ..	±3.0	6 to 120	0.4
Tin ..	±3.5	0.5 ₈ to 11	0.5 ₈
Zinc ..	±2.4	0.2 to 4‡	0.002
Calcium ..	±3.5	0.3 ₈ to 7‡	0.06
Strontium ..	±3.0	0.3 to 6‡	0.04
Barium ..	±3.0	0.5 to 10	0.5

* This concentration range was obtained by using the instrumental conditions given in Table I. A higher concentration of metal in wool than the maximum given here can be accommodated, by rotating the burner more, by using a less sensitive resonance line or by dilution.

† Obtained by using conditions for maximum sensitivity.

‡ The range depended on the dilution used. The values given were obtained by diluting 1 part to 100 parts (for zinc), to 50 parts (for calcium) and to 10 parts (for strontium).

Thus samples of about 0.1 g gave reproducibilities of about ± 8 per cent., whereas samples of about 0.3 g gave reproducibilities of about ± 3 per cent. (see Table II). Larger samples did not give better reproducibility.

PRESENCE OF SOLID MATTER—

The method used to prepare the samples gave dark brown solutions containing finely suspended matter that arose largely from decomposition of the amino-acid, tryptophan. However, neither the average absorbance reading nor the meter fluctuation at this reading was altered after filtration through a Millipore filter (0.20 μ).

ACCURACY AND REPRODUCIBILITY—

Wool was analysed independently for calcium, chromium, copper and zinc. The results, shown in Table III, indicated that the agreement between atomic-absorption spectroscopy and the independent method was good. The reproducibilities of the analyses, determined by analysing the same sample of wool six times, were generally about ± 3 per cent. (Table II). The concentration ranges of metal in wool for which the method is applicable are shown in Table II.

TABLE III
COMPARISON OF ATOMIC-ABSORPTION AND ALTERNATIVE METHODS OF ANALYSIS

Metal	Independent method of analysis	Metal content, mg per g of dry wool	
		Independent method	Atomic absorption
Calcium ..	Nitric acid extraction; EDTA titration	0.068	0.069
Chromium ..	Wet ashing; iron(II) titration of chromium(VI)	9.8	10.0
Copper ..	Hydrochloric acid extraction; EDTA titration	8.0	8.1
Zinc ..	Wet ashing; EDTA titration	5.5	5.5

EFFECTS OF DIFFERENT MEDIA—

As in the determination of aluminium in wool,¹ it was found that the absorbance values in water, constant-boiling hydrochloric acid and wool hydrolysate solutions were in each instance different. This was shown to be largely because of the different surface tensions and viscosities of the solutions, which emphasised the need for samples and standards to be prepared in identical media. This was achieved automatically with the method of standard additions, and with the calibration-graph method by preparing the standard solutions in wool hydrolysates.

VALIDITY OF THE METHOD OF STANDARD ADDITIONS—

The method of standard additions, as normally used, requires a linear relationship between absorbance and concentration. Although this relationship was not linear for calcium in water when a nitrous oxide - acetylene flame was used, it was linear in wool hydrolysates in the concentration range 0 to 8 p.p.m. of calcium.

Willis⁴ has pointed out that the method of standard additions is based on the assumption that the interfering substance alters the absorbance of the added metal to the same extent as it does that of the original sample. This may not always be so, particularly when only a small amount of interfering substance is present, but this condition was established in the present work by making two separate additions to each sample, thus providing a check on the linearity of the analysis in the presence of the interfering material. Although errors caused by instrumental drift are minimised, by measuring in quick succession solutions that are effectively sample and standard, the method of standard additions involves an extrapolation, which makes it inherently less accurate than the calibration-graph method, which involves an interpolation. It is, therefore, essential to correct for the background absorbance, which is caused either by absorbance by the flame or scattering of the light by solid particles in the flame, by measuring the absorbance at a nearby wavelength that is known not to be absorbed by the metal ion under examination. Modulated atomic-absorption apparatus should be used to avoid measuring flame emission.

SCOPE OF THE METHOD—

The results obtained confirm the conclusions drawn from the earlier work¹ that metals in wool can be readily determined by atomic-absorption spectroscopy. The method should be equally suitable for other insoluble protein materials, such as hair and hide. The advantage of being able to use a hydrolysis technique to decompose the protein material, rather than the more lengthy ashing or extraction techniques will still apply. This procedure has the additional advantage, as far as the biochemist is concerned, that the hydrolysate could also be used for other determinations, such as those involved in an amino-acid analysis.

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