

# THE DETERMINATION OF MAGNESIUM IN MOLASSES BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

By V. A. SOFFIANTINI

*Hulett's Research and Development*

## Abstract

A method is described for the quantitative determination of magnesium in cane molasses using a Beckman Atomic Absorption Spectrophotometer. Chemical interferences can be overcome by the addition of lanthanum. The use of a nitrous oxide-acetylene flame with a laminar flow burner is recommended. The precision and accuracy of the method were investigated using recovery and reproducibility tests. A good correlation was obtained between magnesium figures obtained by atomic absorption and by EDTA titration.

## Introduction

Atomic absorption is the conversion of the elements of chemical compounds to atoms and the absorption of the radiant energy by those atoms. During the absorption of the radiant energy, which is in the form of very narrow absorption lines, outer valence electrons of the atoms are excited and move to the next higher energy level. A full discussion on

the theory and application of atomic absorption is given by Robinson<sup>14</sup>.

Atomic absorption spectroscopy was developed some 15 years ago. In 1960 there were over 180 AA instruments in use in South Africa in academic and industrial research as well as for routine analysis in metallurgy, agriculture, clinical and other fields. The Jubilee edition of *Scientia*<sup>4</sup> reports that South Africa is soon to start the local manufacture of hollow cathode lamps.

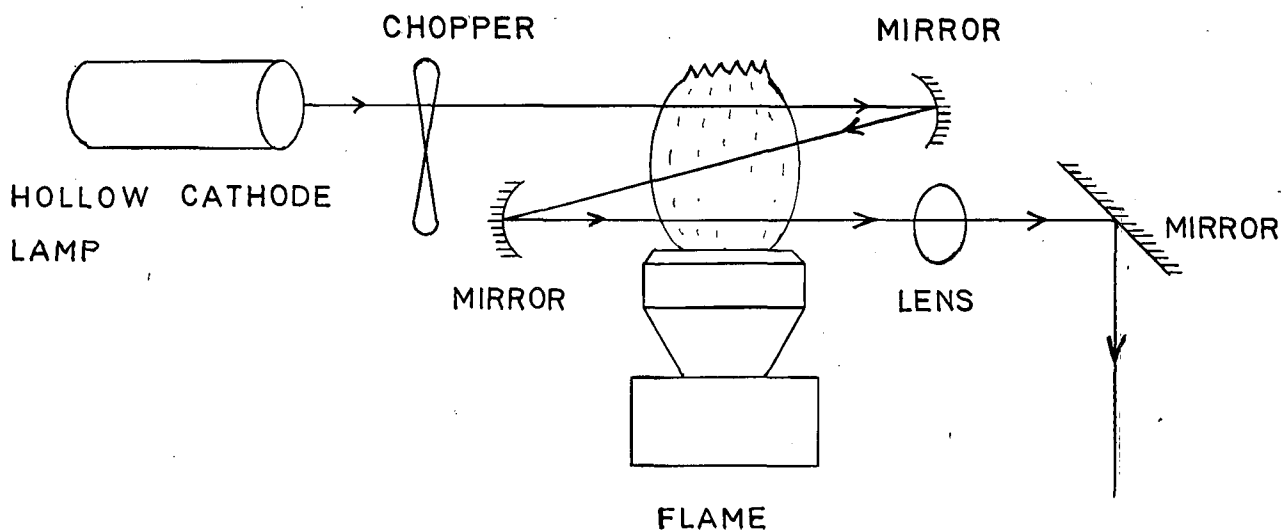
An investigation was undertaken to determine the most efficient burner, flame and mode of operations for the determination of magnesium in cane factory molasses.

Basically, the atomic absorption technique used can be described as follows: As the sample is sprayed into the flame and atomized, a modulated light beam from a specific hollow cathode lamp, at one of the characteristic wavelengths of the element to be analysed, is directed through the flame, on to a grating monochromator and through a slit on to

FIGURE 1

## TRIPLE PASS MODE

FROM BECKMAN BULLETIN NO. 7106



a photomultiplier tube (as detector) which measures the final intensity of the beam.

The number of atoms capable of absorbing any transmitted light is proportional to the product of the concentration of these atoms in the flame and the length of the light path through the flame.

After metals in the sample have been reduced to neutral atoms in the flame (the flame acts as an atomizer) they stay in this state for varying periods of time. This time period is ended if, and when, the atoms become oxidised.

The use of nitrous oxide as the oxidant decreases the probability of the metal atoms becoming rapidly oxidised in the flame. A nitrous oxide acetylene flame requires the use of a laminar flow burner to assure maximum atomization.

The triple pass mode, which increases the length of the light beam through the flame threefold (see Figure 1) can be used to improve the sensitivity of the instrument when working with low concentrations. On the laminar flow burner the hot mode operation increases the sensitivity tenfold when working with low analyte concentrations. A general expansion of the signal may also be achieved by coupling the instrument to a Beckman Potentiometric Recorder incorporating a Scale Expansion Accessory. This scale expansion can only be used when the noise level of the signal is low.

Lewis<sup>10</sup> compared various other analytical methods with atomic absorption spectrometry and reported errors due to contamination and losses in working with very dilute solutions.

Any process that affects the atomic concentration in the flame affects flame emission and AA measurements to the same extent. However, the lack of interference from excitation effects is one of the inherent advantages that AA has over emission procedure.

For any given cation different anions form compounds with different stabilities. This directly affects the production of neutral atoms in the reduction step of atomic absorption spectrometry. Variations, if present, in the intensity of the light source in AA analyses, can be overcome by using double-beam instrumentation where the ratio of the sample and

reference beams are measured. Although the spectrophotometer used has internal double-beam optics, the AA system used in this investigation operates on the single beam principle. The light source is modulated to overcome any radiation interference from the flame.

Marks and Welcher<sup>12</sup> have reported that in interelement interference in atomic absorption analyses with nitrous oxide-acetylene flames, the volatility of the solvent in terms of boiling point and heat of vaporisation is not necessarily of prime importance but that the volatility of the analyte is in some manner increased or decreased by the presence of other accompanying chemical constituents. Many interferences can be reduced or eliminated by the proper selection of flame conditions and instrumental variables (Fassel and Becker<sup>6</sup>, Marks and Welcher<sup>12</sup>).

High sodium concentrations are the most frequent interfering concomitants in many natural products analysed by atomic absorption and flame photometry. Although a decrease in signal in the presence of high concentrations of NaCl has been reported (Ramirez-Munoz<sup>13</sup>), it has been stated that magnesium can be determined with a laminar flow burner and hot mode operation even in the presence of high concentrations of sodium chloride.

Carpenter and Bichsel<sup>3</sup> have investigated the determination of trace metals in process juices and white sugars using an Aztec total consumption air-acetylene burner head. They used an approximately 5 brix solution for beet molasses to avoid interference problems. However, they reported that some interferences were encountered in the determination of magnesium; these were eliminated with the addition of lanthanum.

### Experimental

The instruments used are a Beckman Model 97900 Atomic Absorption unit coupled to a Beckman DB-G Spectrophotometer. The characteristics of the Beckman Laminar-Flow Burner, catalogue number 105550 are shown in Table I. A Beckman hollow cathode lamp was used as a source for magnesium determination.

TABLE I  
Characteristics of Beckman laminar flow burner, Cat. No. 105550

Fuel	Oxidant (support gas)	Flame Characteristics		Type of Flame Atomizer	Function	Characteristics	Consumption Rate of Sample
		Type	Temp				
Acetylene	(i) Nitrous Oxide (ii) Air	Premix	(i) 3 000°C	Discharge Burner (Lundegardh)	Sample is nebulized. Proportion of solvent is removed by I.R. heat (hot mode) fuel is injected and mixture ignited at slot.	1. Sensitivity improved by the elongated burner. 2. Large droplets eliminated 3. In mixed solvents, the more volatile solvent is evaporated first. 4. Silent operation (but subject to loud flashback explosions if blocked or operated incorrectly due to the mixture of unburned combustible gases.)	1,5 ml. per minute with small bore capillary (cold mode)  3,5 ml. per minute with large bore capillary (hot mode).
			(ii) 2 200°C				

Sintered glass atomizer filters have been inserted into the nitrous oxide and acetylene gas lines to prevent the clogging of the burner which can lead to flashback. Another precaution taken has been to replace acetylene gas cylinders when the pressure falls below  $2,8 \text{ kg cm}^{-1}$ . Below this pressure other substances such as acetone may enter the flame and could cause interference (Dean<sup>5</sup>).

Magnesium standards are prepared from 100 ppm aqueous solutions of the metal chloride. Analytical grade chemicals and grade A glassware are used throughout.

The chloride was chosen in order to compensate for any anion interference since the concentration of chloride in cane molasses is, on average, higher than that of any other anion (MacGillivray and Matic<sup>11</sup>). Deionised water is used for all dilutions, and solutions are stored in polyethylene containers to reduce the risk of contamination.

A 10% solution of lanthanum is prepared by dissolving 23 g of  $\text{La}_2\text{O}_3$  in a minimum (25 ml) of nitric acid and diluting to 200 ml with deionised water. 0,15% of lanthanum is added to all blanks, standard and samples.

Five grams of factory molasses, (with other materials different solution concentrations must be used), are dissolved in hot deionised water, cooled and diluted to 200 ml, 1 ml aliquots of this solution are treated with 1,5 ml of the lanthanum stock solution and diluted to 100 ml, so that the concentration of the element being measured in the diluted sample falls within the analytical range of the instrument. (Spectrophotometer scale readings are generally taken to be accurate in the range 10% to 80% transmission.)

The absorption signals of the blanks, standards and test solutions are measured as absorbance, operating the instruments as described in the manufacturer's handbook<sup>1</sup>. To lessen any spectral interference the smallest slit width possible under maximum gain control is maintained at all times. The recommended gas pressures are applied to obtain optimum flow rates to produce maximum atom population in the flame. (The instrumental and analytical parameters are shown in Table II.)

TABLE II  
Instrumental and analytical parameters

Analyte	Magnesium
Burner	Laminar
Technique	Absorption
Flame	$\text{N}_2\text{O}$ -acetylene
Mode of operation	Hot mode
Optics	Triple pass
Resonance wavelength	285,2 nm
Lamp current	20 mA
Slit width	0,03 mm
Burner height	Level
Oxidant pressure (nitrous oxide)	18 psi
Fuel pressure (acetylene)	8 psi
Sensitivity*	0,001 ppm
Analytical range	0,2 to 3,0 ppm

\*Sensitivity is defined<sup>14</sup> as 'that concentration of solution that will lead to one per cent absorption when atomised in a flame'. The sensitivity figures quoted in this table are taken from the Beckman bulletin<sup>2</sup>.

A typical calibration curve is shown in Figure 2. A new calibration curve is drawn for every series of analyses carried out.

### Results and discussion

The effect of the use of lanthanum was illustrated by two series of comparative magnesium determinations, with and without the addition of interference buffers. In the second series, blanks, standards and samples were treated with 0,15% of lanthanum as the amount of lanthanum present should not be less than the concentration of the sample. The results of the comparisons, recorded in Table III, show clearly the effects of the addition of the lanthanum. The effect of the addition usually increases the reported quantity of magnesium. The size and direction of the effect of the lanthanum will depend upon the nature of the interfering substances.

TABLE III  
Addition of lanthanum

Sample Code	Ash %	ppm magnesium in molasses		
		No lanthanum	0,15% lanthanum	Difference
EM 2	15,72	6 000	6 000	0
FX 1	15,94	6 100	6 400	+ 300
AK 4*	15,52	6 280	6 800	+ 520
AK 5	15,91	6 100	6 660	+ 560
FX 5	16,14	6 000	6 580	+ 580
EM 1*	15,60	6 000	6 600	+ 600
EM 3	15,85	5 400	6 000	+ 600
TS 1*	15,20	5 360	6 000	+ 640
AK 1	16,50	6 100	6 800	+ 700
AK 2	16,43	6 100	6 800	+ 700
EM 4	15,66	5 400	6 100	+ 700
FX 4*	16,34	6 240	7 000	+ 760
AK 3	16,14	6 000	6 800	+ 800
FX 6	15,23	4 900	6 000	+1 100
FX 2*	15,58	5 900	7 000	+1 100
FX 3*	16,38	5 900	7 200	+1 300

\*The ash figures, which are reported for purposes of comparison, were obtained by the double sulphatation method<sup>9</sup>. Asterisks indicate data which also appear in Table VI.

Recovery tests were carried out using the "method of standard addition". Varying amounts of the 100 ppm stock solution were added to the diluted molasses sample and all solutions treated with lanthanum. The results which are shown in Table IV, indicate that recovery of the added magnesium was satisfactory.

The reproducibility of the proposed method was investigated. Six 5 g portions of a molasses sample

TABLE IV  
Magnesium recovery tests

Quantity Added	Theoretical Total	Experimental Total	Per cent Recovered
0	—	1,63 ppm Mg	—
0,5 ppm Mg	2,13 ppm Mg	2,10 ppm Mg	94
1,0 ppm Mg	2,63 ppm Mg	2,64 ppm Mg	101
1,5 ppm Mg	3,13 ppm Mg	3,14 ppm Mg	101

were weighed and the magnesium contents determined by the method described including the addition of lanthanum. The reproducibility test was repeated 48 hours later using the same solutions but with a new calibration curve. The results are shown in Table V. The standard deviation, 0,032% was 5,1% of the mean concentration, 0,63% Mg. This altered to a standard deviation of 0,035%, 5,7% of the 0,61% Mg mean concentration, 48 hours later.

**TABLE V**  
Reproducibility tests

Aliquot Number	Magnesium Per cent	
	Direct	After 48 hours
1	0,58	0,58
2	0,63	0,60
3	0,63	0,60
4	0,68	0,68
5	0,63	0,60
6	0,63	0,60
Mean	0,63%	0,61%
Standard deviation	0,032%	0,035%

The determination of magnesium by atomic absorption was compared with the standard methods using EDTA (Vogel<sup>17</sup>). The molasses was pretreated by wet-ashing three times with hydrochloric acid, followed by ignition at 600°C. ICUMSA<sup>8</sup> tentatively recommended a pretreatment for molasses involving wet-ashing with a mixture of perchloric and nitric acids, but this treatment produced complications. The calcium magnesium was determined by EDTA titration using Eriochrome Black T as indicator. Calcium alone was determined, also by EDTA titration, using Patton and Reeders indicator, and the magnesium content calculated by difference. The results are summarised in Table VI. The maximum difference between the results by the two methods was 5% of the value determined by EDTA, the mean deviation was 3%.

Although it had been reported (Shifrin, Hell and Ramirez-Munoz<sup>18</sup>), that the sensitivity for magnesium at 285,2 nm was poorer in the nitrous oxide-acetylene flame than in an air-acetylene flame, tests with a fuel-lean air-acetylene flame were abandoned because of poor reproducibility using standard magnesium solutions, probably due to background interference.

Possible interferences in the determination of magnesium by atomic absorption include those of aluminium, phosphates and sucrose. The suppressive interference of aluminium is known to be eliminated by the use of a nitrous oxide-acetylene flame or by the addition of strontium or lanthanum to the solution. The interferences of calcium was examined by adding 30 ppm Ca to magnesium standards ranging from 0,3 ppm to 3,0 ppm. As can be seen from Figure 2, calcium had little effect on magnesium results obtained using nitrous oxide-acetylene flame, hot mode, with triple pass. Other interferences are lessened or eliminated by the addition of lanthanum (Robinson<sup>14</sup>) in excess of the concentration of the interfering ions.

Comparison of the results of Table III and VI show that the figures obtained by atomic absorption after the addition of lanthanum are far closer to the analyses by EDTA titration than are the figures obtained by AA without using the interference buffer.

**Conclusions**

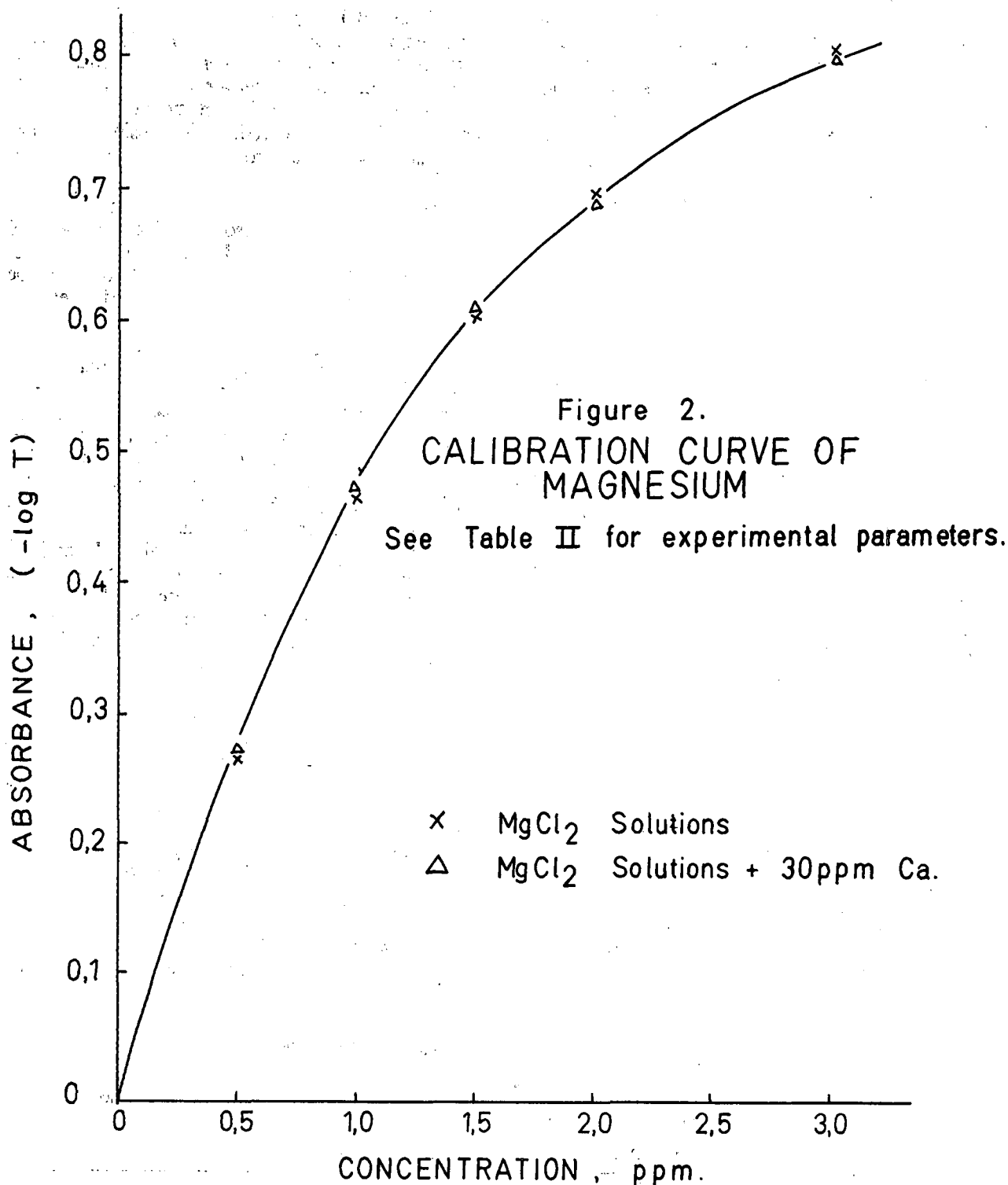
The magnesium content of cane factory molasses can be determined satisfactorily by atomic absorption using a nitrous oxide-acetylene flame and a laminar flow burner. Lanthanum must be added to all solutions to minimise interference. No lengthy pretreatment is required and the total time taken for the analysis is much shorter than for gravimetric or compleximetric determinations of the metal. The method is sufficiently precise and reliable to be suitable for use on a routine basis (Soffiantini *et al*<sup>16</sup>).

It should be remembered, however, that there are

**TABLE VI**  
Comparison between atomic absorption and EDTA methods

Sample Code	Ash %	magnesium ppm			Difference % $\frac{100(b-a)}{a}$
		(a) by EDTA	(b) by AA	(b-a)	
DL 3	16,03	6 920	6 900	20	0,28
EM 1*	15,60	6 540	6 600	60	0,91
EM 6	14,52	7 020	6 900	-120	-1,70
DL 1	15,89	7 260	7 100	-160	-2,20
DL 2	15,96	7 070	6 900	-170	-2,40
TS 1*	15,20	6 190	6 000	-190	-3,06
FX 3*	16,38	6 990	7 200	210	3,00
AK 4*	15,52	6 570	6 800	230	3,50
DL 4	16,08	7 150	6 900	-250	-3,49
FX 4*	16,34	7 280	7 000	-280	-3,84
FX 2*	15,58	7 340	7 000	-340	-4,63
					Mean difference 2,63

\*Asterisks indicate data which also appear in Table III



various factors which adversely affect the atomic absorption signals, such as unnoticed changes in gas flow rates and aspiration rates. These can be neutralised by adopting the method of internal standardisation which is discussed by Feldman<sup>7</sup>. An additional drawback is that any error in sampling and preparation will be greatly magnified because of the large dilution used in the atomic absorption technique. These errors should be minimised by using A grade glassware and highest quality chemicals, and by very strict attention to detail. In this regard it is recommended that a new set of standards should be analysed concurrently

with every batch of samples, and a new calibration curve prepared for each set of determinations.

It is generally known that the use of organic solvents enhances the atomic absorption signals. The use of solvents in the determination of metals in molasses is a possible avenue for future research.

#### Acknowledgements

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Figure 1 is a simplification of an illustration in a Beckman bulletin and is reproduced by kind permission of Beckman Instruments (Pty) Ltd.

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#### Discussion

**Dr. Matic** (in the chair): The great advantage of this method is that no lengthy pre-treatment of the material is required. Errors that occur will mainly be due to the dilution necessary to bring the particular elements to the very low concentration at which the instrument operates.

A triple pass instrument was used, which has been developed to work at very low concentrations in order to increase the signal. This may not be quite suitable for the purpose for which you want to use the instrument because of the additional dilution required.

**Mr. Teokarovic:** When making a standard solution of magnesium chloride the metal must be completely

pure and owing to possible absorption of the solution by the glass container the solution must be used fairly soon after being prepared.

The very wide variation of results in Table III is probably due to the presence in the molasses of calcium, potassium and sodium.

**Mr. Soffiantini:** There are suppliers from whom it is possible to obtain specific standard solutions for atomic absorption.

The reason 0,15% of lanthanum was used, was that for other molasses samples such as HTM and refinery molasses the same quantities can be used by only increasing the sample aliquot.

**Mrs. Dunsmore:** The S.M.R.I. has a Techtron atomic absorption spectrophotometer, not a Beckman.

No high temperature flame was necessary as the acetylene/air flame was sufficient and gave excellent recovery but at no time was there agreement between EDTA and AA—the AA always being higher. This of course may be due to the different instruments.

**Mr. Soffiantini:** A research worker in atomic absorption must specify what type of instrument he is using as each has its own characteristics. I have tried air/acetylene which is a relatively cooler flame than the nitrous oxide/acetylene flame, using the Beckman laminar flow burner. However the results were not reproducible, possibly due to background absorption.

The correlation between EDTA and AA depends on the pre-treatment of the molasses. I used wet ashing with hydrochloric acid and results compared favourably with the AA method. There are two titrations with different indicators and I found the end point difficult to detect. Of course some operators may be colour blind and one will be unable to detect the same end point as another.

**Mrs. Dunsmore:** The titration is difficult owing to the instability of the organic indicators.

**Mr. Cox:** I understand that a graphite arc can be used for very high temperature applications. If the ionic state of these atoms is important the temperature would possibly be too high because you are measuring the quantity of energy produced. In an electrical furnace there would be considerable stripping of the outer electron from the atom and there would be interference with the quantity of energy that would be absorbed.

**Mr. Soffiantini:** Some research workers pass the inert gases through the furnaces and this tends to eliminate that effect to some extent.

**Mr. Cox:** Would you be getting to the order of plasma conditions where there would be a great deal of stripping?

**Mr. Soffiantini:** Yes, but you must remember that in AA we do not want ionisation to take place—we want excitation to take place, which is different.

**Dr. Murray:** The AA effectively reduces all the magnesium, both the complex and the inorganic and organic, to find how they are split in the two forms? The specific properties of the molasses will depend on inorganic or organic form of the molecules which occur.

**Mr. Soffiantini:** This is an avenue for future research.

**Dr. Matic:** The viscosity of the solution sprayed into the flame plays a big part in determination by atomic absorption. Has an effort been made to gauge the effect of sucrose on the determination? Also, have you tried adding to your standard solution the most common impurities known to be present in various factory products to see what kind of recoveries are obtained.

**Mr. Soffiantini:** The viscosity of the solution sprayed into the flame plays a big part in determination by atomic absorption. Has an effort been made to gauge the effect of sucrose on the determination? Also, have you tried adding to your standard solution the most common impurities known to be present in various factory products to see what kind of recoveries are obtained.

**Mr. Soffiantini:** The literature states that only phosphates and aluminium, and possibly sucrose, tend to interfere.

Carpenter and Bichsel who analysed magnesium in beet molasses state in the paper that they found no interference from sucrose, especially when using a very dilute solution of less than five brix. In a stronger solution there might be interference from sucrose.

**Mr. Cox:** In determining magnesium the impurities included are aluminium, phosphate and sucrose. Is it possible to screen out interference from these two substances without the introduction of a better

wavelength selector, or is this a difficulty that is inherent in the AA method?

**Mr. Soffiantini:** In AA there are chemical as well as spectral interferences.

Magnesium will also absorb at a wavelength of 279,6 nm. This is not a resonance wavelength but it will absorb at this wavelength. Manganese will also absorb at 279,5 nm, a difference of 0,1 nm. If the instrument uses a prism for a monochromator instead of ordinary filters there will be less interference.

Another way to eliminate spectral interference is to use a smaller slit width, the smallest possible under maximum gain control.

**Mr. Cox:** The chemical interference would seem to be due to too cool an atomising flame.

If you get ideal atomisation it should be possible to eliminate most of the interference.

**Dr. Murray:** I notice that phosphate is regarded as a possible source of interference so how do you overcome this?

**Mr. Soffiantini:** The paper by Carpenter and Bichsel states that the use of lanthanum is sufficient to suppress the influence of phosphate.

**Dr. Matic:** Mr. Soffiantini does not claim, nor does the S.M.R.I., that 100% accurate results are obtained, but the errors are about the same as if determined by any other method. The method is however fast, simple and gives acceptable.