

THE BEHAVIOUR OF CERTAIN ELEMENTS IN THE ABSORPTION TUBE

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ABSTRACT

The considerations and conclusions presented are based mainly on the use of a total consumption nebulizer burner in conjunction with a non-polished silica absorption tube about 45 cm in length and internal diameter about 10 to 15 mm.

The main object of the study is to examine the effect of gas composition in the tube on various elements, e.g. alkali, alkaline earth and transition elements as well as certain mysterious elements such as tin and molybdenum. Atom profiles in the tube are compared with atom distribution in common premixed flames.

The effects of the cell material and its shape on the absorption background and the various types of memory effects are also considered and suggestions are made for their elimination. Some interesting instances of molecular absorption are presented together with the application of the absorption tube for routine analysis of trace elements in geological samples.

GENERAL

The common feature of all absorption cells is that they confine the absorption medium into a cylindrical form along the longitudinal axis through which the absorbed light passes (*Figure 1*).

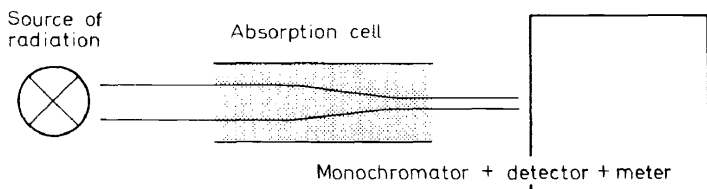


Figure 1. General scheme of an absorption cell

Compared with the conventional arrangement with a freely burning flame the cell is distinguished basically by a prolonged optical path. Also of importance is protection of the admixture from the outside atmosphere, which makes it possible to prepare well-defined gas mixtures and to increase the concentration of free atoms in the absorption medium.

The absorption medium in the cell can be prepared using either flame and/or non-flame sampling, by which both solid and liquid samples are atomized.

If we consider absorption cells from the historical point of view we must

not forget that this technique was in fact the first analytical use of atomic absorption spectroscopy—namely by Woodson for the determination of mercury in the late 'thirties¹. After introduction of atomic absorption for general use Robinson was the first who applied the absorption tube technique² in 1962 (*Figure 2*). He used a T-shaped flame adaptor of silica glass together with a total consumption burner and succeeded in increasing tenfold the sensitivity of the determination of platinum. Later, he used this adaptor in conjunction with the Perkin-Elmer Model 303 and determined further elements.

Most popular is the scheme used by Fuwa and Vallee³ with a long Vycor tube into which the flame from a Beckman burner had been introduced (*Figure 3*). By this device they and various other authors^{4,5} were able to increase considerably the sensitivity of determination of fifteen elements.

Kirkbright *et al.*⁶ used another approach. They led the interconal gases of a premixed air-acetylene flame into a heated cell (*Figure 4*). With the use of

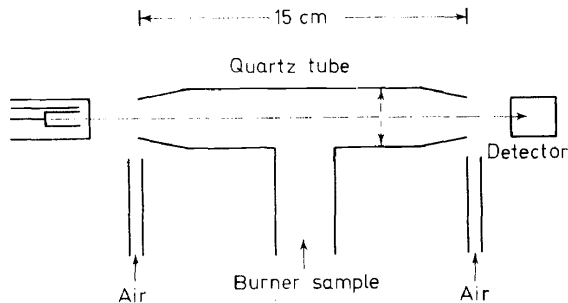


Figure 2. Flame adaptor of Robinson²

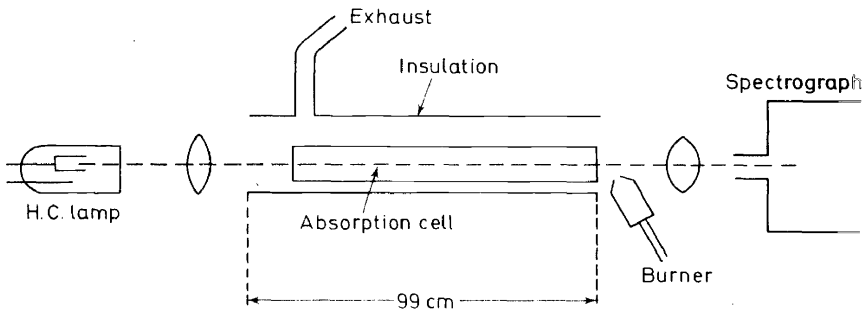


Figure 3. Absorption tube of Fuwa and Vallee³

this long-path burner the detection limits were improved, mainly by lowering flame noise, the sensitivity being almost the same as with the conventional arrangement.

As we are interested in devices using flame sampling I shall not refer to the absorption cells by Lvov, Massmann and others. Mention should be made, however, of promising methods using both pneumatic and ultrasonic nebuli-

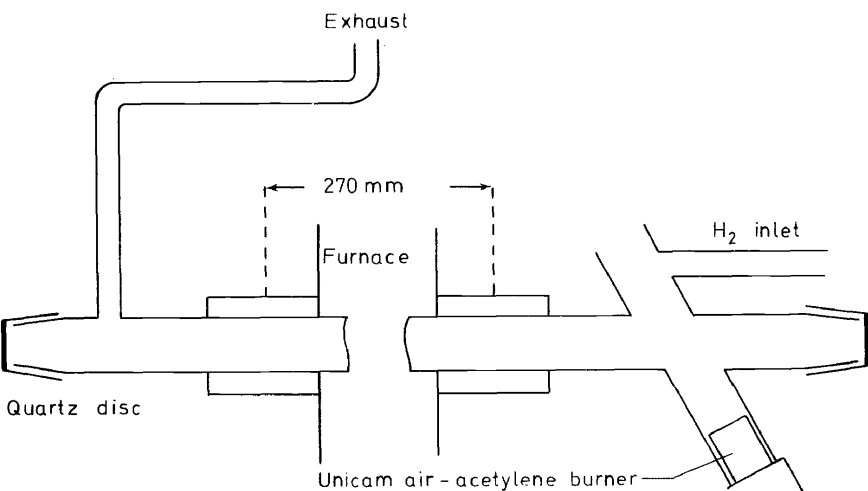


Figure 4. Absorption cell of Kirkbright⁶

zers from which the aerosol is led directly to the tube, as used, for instance, by Mislán⁷ or Woodriff⁸.

Summing up the history of spectroscopic absorption tube techniques it can be stated that many different approaches were examined but that all were—perhaps with the partial exception of Lvov's work—of a preliminary nature, lacking thorough investigation and exploitation of all possibilities. Except for the determination of mercury the cell technique has not been commercially utilized although published results so far are favourable. In my opinion this situation does not imply inefficiency of the technique—I certainly hope it is not—but the difficulty of both theoretical and experimental problems. This article presents a brief summary of the current state of the method.

EXPERIMENTAL ARRANGEMENT

We have been working on this problem for about five years, using an arrangement similar to that of Fuwa and Vallee with a heated tube (Figure 5).

For most experiments we used hollow cathode lamps of various makes fed by a d.c. stabilized supply. The light from the lamp was focused by a lens into the entrance end of a raw silica tube, 45 cm long with 13 mm inner diameter. The tube was heated in an electric furnace 38 cm long. The temperature distribution in a heated and unheated tube is shown in Figure 6. The flame from a Beckman 4020 burner, operated on air and hydrogen, was introduced into the tube. The burner mouth is 8 to 10 mm from the tube end, the tube and burner generally forming an angle of 45°. The light beam from the tube is focused on to the entrance slit of the monochromator by a sphericylindrical lens. The monochromator was a Zeiss instrument with a prism. We used the simplest d.c. system; the photocurrent from the multiplier was measured by a

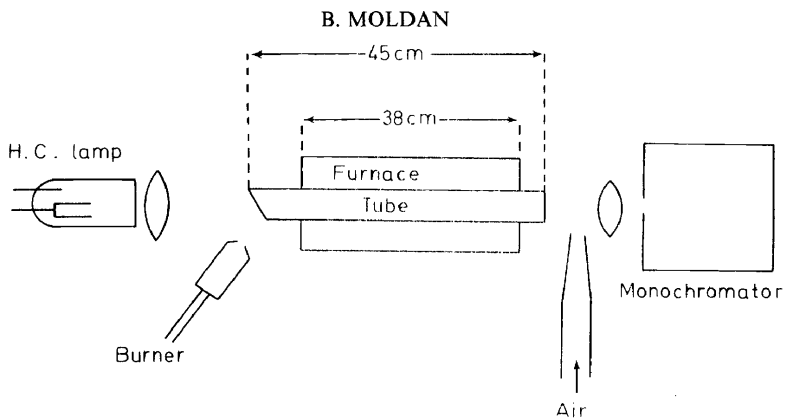


Figure 5. Experimental arrangement used in our laboratory

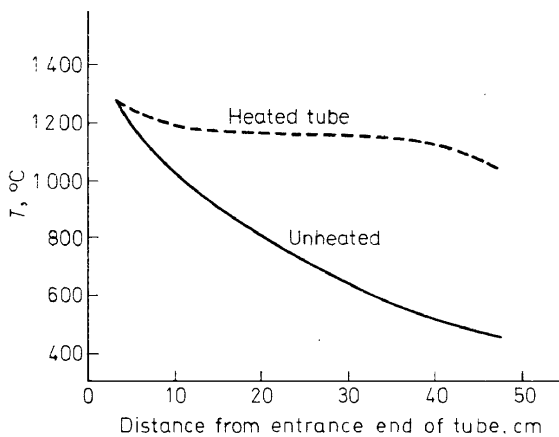


Figure 6. Temperature in the tube

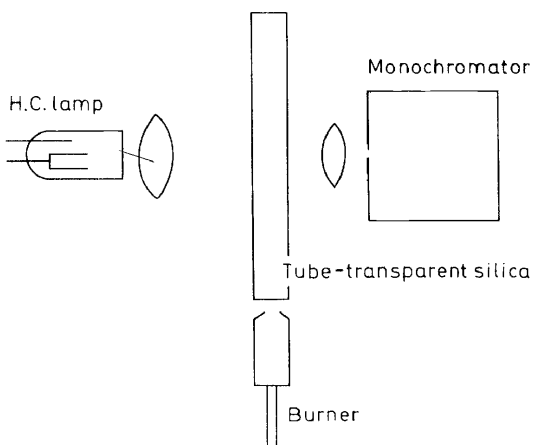


Figure 7. Experimental arrangement for measuring absorption profiles

The elements studied (*Figure 8*) can therefore be roughly distributed into two main groups: elements whose oxides have dissociation energies smaller than the dissociation of the OH radical (100 kcal/mol), and elements with greater dissociation energies.

According to the relative values of the boiling points of the oxides and the temperature of the air-hydrogen flame the so-called 'successful' elements can be further divided into two groups (*Figure 9*). I will now briefly outline the behaviour in the absorption tube of these three groups of elements.

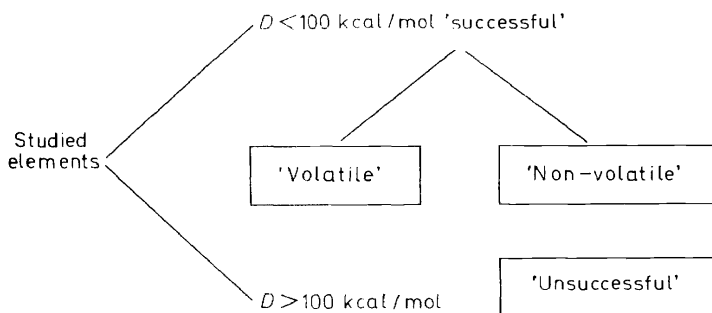


Figure 9. Division of the elements studied

Volatile elements

Out of the volatile element group (*Figure 10*) we have studied sixteen elements, most of which are often determined by atomic absorption.

The data on sensitivity for one per cent absorption are given in *Table 1*.

Na						
K	Cu	Zn			As	Se
	Ag	Cd	In		Sb	Te
	Au	Hg	Tl	Pb	Bi	

Figure 10. Volatile elements

Table 1. Sensitivity of volatile elements

Element	Line	Sensitivity p.p.m.	Factor	Element	Line	Sensitivity p.p.m.	Factor
Na	589.0	0.001	30	In	303.9	0.05	20
K	766.5	0.002	25	Tl	276.8	0.02	25
Cu	324.8	0.0075	14	Pb	217.0	0.005	80
Ag	328.1	0.002	50	As	197.2	0.25	15
Au	242.8	0.01	30	Sb	217.6	0.025	40
Zn	214.0	0.001	30	Bi	223.1	0.025	40
Cd	228.8	0.001	30	Se	204.0	0.25	20
Hg	253.7	0.03	170	Te	214.3	0.025	40

The 'factor' in the last column is only an orientation figure which shows the enhancement compared with the conventional arrangement with the 12 cm air-acetylene flame. The sensitivity achieved on our device was compared with the average values given for the following instruments: Perkin-Elmer 303, Techtron AA4 and Unicam SP90.

From the dependence of relative absorption on the hydrogen flowrate the mechanism of the atomization processes occurring in the tube may be inferred. Typical curves are given in *Figure 11*.

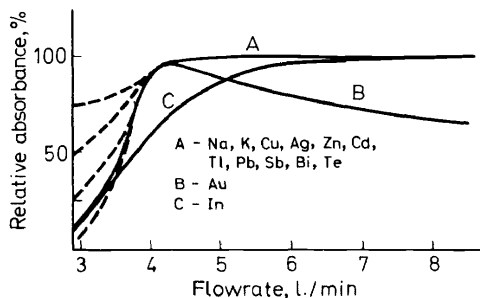


Figure 11. Dependence of relative absorbance on hydrogen flowrate of volatile elements

The flowrate of air is 4.2 l./min. As we do not know the exact volume of entrained air, we can only assume that at the value of about 4 l./min of hydrogen the flame becomes stoichiometric and above this value it is fuel-rich. There is an analogy with a split premixed flame because in this case a second reaction zone appears at the exit end of the tube. The curves were measured with concentrations exceeding by about 20 to 50 times the sensitivity value.

Curve A is characteristic for elements whose compounds are dissociated at the point where the flame becomes fuel-rich. Once free atoms appear, no compounds are formed with the combustion gases and the concentration of free atoms does not change. The dotted lines on the left part of the curve represent possible cases for elements having different ratios between absorption in fuel-lean and in fuel-rich flames. This ratio is in rough correlation with the dissociation energies of the respective oxides. That means the elements with the lowest ratio, e.g. Ag, correspond to the upper line, elements with higher ratios have the lower lines.

Curve B is the case of elements which form compounds with the flame gases, most probably hydrides.

Curve C was obtained with indium for which the most stable compound is not the oxide but the hydroxide. Therefore, its maximum concentration in the air-hydrogen flame is achieved only after the concentration of OH radicals is diminished. According to our measurements of OH band absorption the maximum concentration of OH radicals is at 4.5 l. H₂/min.

The distribution of free atoms along the tube was measured by scanning the absorption profiles of the tube. The disadvantage of this measurement was the fact that the tube was not heated so that the lifetime of free atoms and the profiles were thus influenced by the temperature drop. Some curves are shown in *Figure 12*.

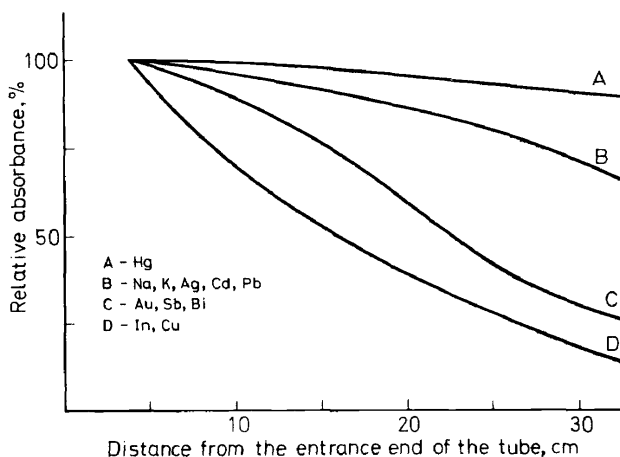


Figure 12. Absorption profiles of volatile elements

In general it can be said that these profiles reveal more about the practical usefulness of absorption tubes for the particular element than about the processes in the tube because the shape of the curves in all cases was almost identical with only their slope altering. When the hydrogen flowrate was changed, the shape of the curves was not affected; the values of measured absorbance, however, changed depending on hydrogen flowrates as shown above.

Most of these volatile elements are not subject to serious interference effects. Roughly summarized, these metals are free of interferences by cations as they would be in the conventional arrangement of atomic absorption. More serious are the effects of anions; sulphates and phosphates in particular have a depressing effect on some of these elements. A characteristic influence of HCl was observed on gold and indium which are both strongly depressed. This is probably due to changes in the reactions in the gaseous phase.

Background absorption can also be considered an interference effect; this will be dealt with later.

In general, for this group of elements the interference effects do not represent a serious problem although they are mostly somewhat higher in the absorption tube than in the conventional flame.

Non-volatile elements

On the basis of somewhat arbitrary classification we include in the non-volatile group: Mn, Fe, Co, Ni, Rh, Pd, Pt. The absorption tube technique proves to be promising for these elements although in general the improvement of sensitivity is smaller than for the volatile elements. Data on the first four of these elements appear in *Table 2*.

D is the dissociation energy of the particular oxides. The dependence of relative absorbance on hydrogen flowrate is shown in *Figure 13*.

From these curves it is clear that the atomization mechanism of the elements is complicated and we can presume the formation of hydroxides, hydrides and other compounds.

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Table 2. Sensitivity of iron group elements

Element	Line	D (kcal/mol)	Sensitivity p.p.m.	Factor
Mn	279.5	94	0.005	20
Fe	248.3	95	0.015	10
Co	240.7	?	0.014	15
Ni	232.0	97	0.016	10

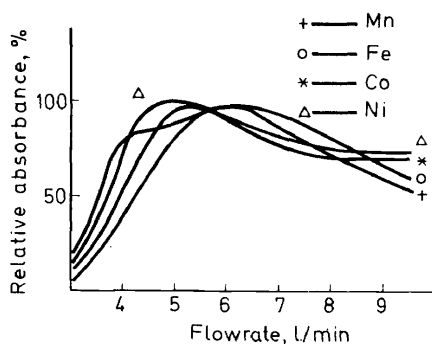


Figure 13. Dependence of relative absorbance on hydrogen flowrate of iron group elements

The absorption profiles of the tube compared with those for the previous group of elements show that for non-volatile elements the effective length of absorption is only about 20 cm. At this point the absorbance invariably drops to five to ten per cent of the maximum value.

As can be expected the interference effects on these elements are very complicated. Some of them (as for example the depressive effect of Al, PO_4^{3+} etc.) are classifiable as condensed phase interference effects and can be partly removed by addition of some releasing agent. But the mechanism of other effects, particularly depressive effects by anions, acids, various cations and mutual interferences is uncertain. In every practical analysis great care must be given to the investigation of these problems.

Very little can be said about the platinum group metals investigated. We also included these in this group because almost no data about dissociation energies, volatility etc. are published. I can present only the results of our measurements. The sensitivities are given in Table 3.

Table 3. Sensitivity of platinum metals

Element	Line	Sensitivity	Factor
Rh	3435	0.02	15
Pd	2476	0.01	80
Pt	2659	0.5	6

In Figure 14 the dependence of relative absorbance on hydrogen flowrate is shown.

From these curves it can be postulated that Pd belongs to the group of

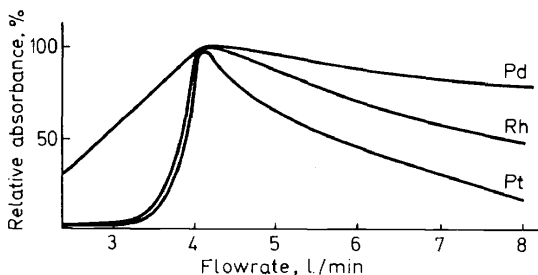


Figure 14. Dependence of relative absorbance on hydrogen flowrate of platinum metals

elements which probably do not form compounds with flame gases while Rh and Pt probably form hydrides.

All elements of this group are subject to many different interference effects by both cations and anions, which were only partly studied. But even these partial results reveal that much more attention should be given to these elements. From the point of view of practical analytical chemistry the use of absorption tubes for determining these effects is interesting because of their low abundance in natural materials.

Elements forming stable oxides

As may be deduced from theoretical considerations, most elements whose oxides have a high dissociation energy cannot be determined with the absorption tube technique especially with the hydrogen-air flame. Therefore, only some 'borderline' elements were investigated. The data obtained on sensitivities are given in Table 4.

Table 4. Sensitivity of the elements forming stable oxides

Element	Line	D (kcal/mol)	Sensitivity p.p.m.	Factor
Mg	285.2	100	0.002	5
Ca	422.7	115	0.16	0.6
Sr	460.7	112	0.16	1
Cr	357.9	101	0.2	0.75
Mo	313.3	116	> 50	—
Ga	287.4	102 (GaOH)	1.2	2
Ge	265.2	150	> 50	—
Sn	224.6	131	0.04	50

The small sensitivity of all elements mentioned above is not surprising even if some authors found better sensitivity for magnesium, which could be expected from the relatively low value of *D*. The absorption profiles of these elements show an abrupt decrease of absorption so that at the point of 10 cm the absorption is diminished to an average of ten per cent.

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What is in fact surprising is the great sensitivity of the determination of tin (*Figure 15*). It is well known that tin and, according to Amos and Willis⁹, germanium also are the only elements from this group whose sensitivity is better in the hydrogen-air flame than in acetylene-air.

Owing to the relatively low boiling point of the tin oxide, tin is completely evaporated in both flames even as oxide. It may be presumed that in the hydrogen flame there exists some mechanism able to dissociate compounds with an even greater dissociation energy than that of the OH radical. But being relatively slow, it would be effective only when all the oxide is in the gaseous state. This would explain the great increase of sensitivity of tin when using absorption tubes. Tin is the only element whose oxide is easily volatilized but with a dissociation energy higher than 100 kcal/mol.

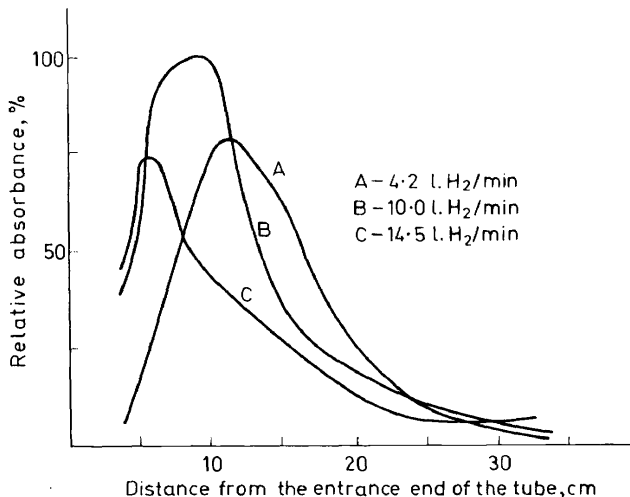


Figure 15. Absorption profiles of tin

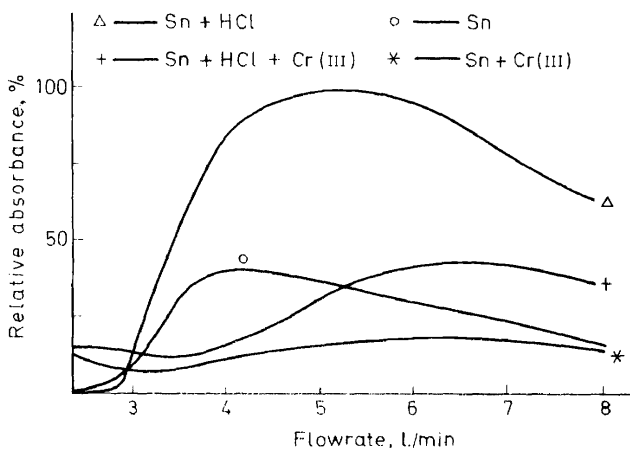


Figure 16. Dependence of tin absorbance on hydrogen flowrate

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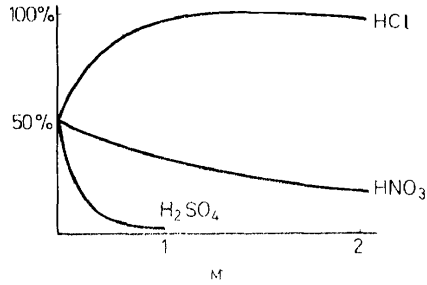


Figure 17. Absorbance of tin in various acids

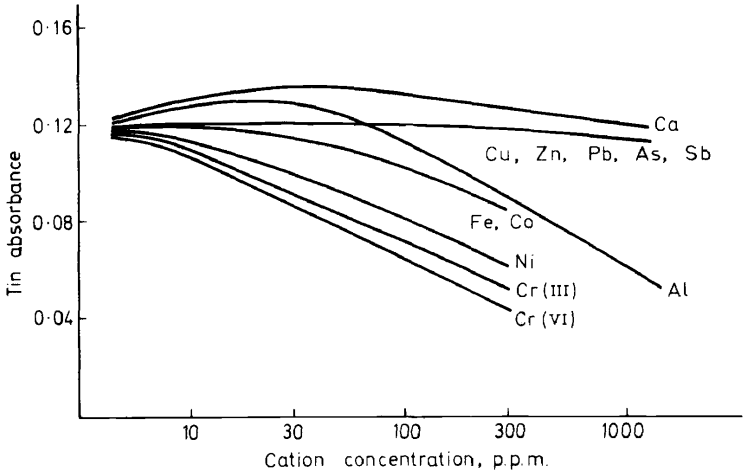


Figure 18. Influence by various cations on tin absorbance

The view that the main atomization mechanism of tin compared with other elements is relatively slow is also supported by the fact that on the absorption profile a distinct maximum is found at a certain distance from the tube entrance. This was the only case observed.

The complexity of tin atomization also follows from the dependences of absorbance on hydrogen flowrate in the presence and absence of hydrochloric acid and chromium. Chromium was found to have the greatest depressive effect as shown in *Figure 16, 17 and 18*. The concentration of tin is 2 p.p.m. in all cases, HCl 1 M, Cr(III) 300 p.p.m. Tin is also subject to various interferences both by anions and cations.

SPECIAL CELL EFFECTS

Background absorption

Background absorption is an important factor when working with an absorption tube. In the presence of some elements or compounds the ab-

sorption spectrum exhibits considerable variation with wavelength suggesting that it is due to absorption of molecular spectra. The results so far published and those obtained in our laboratory confirm this presumption. In the last paper published by Fuwa and Vallee¹⁰ molecular absorption

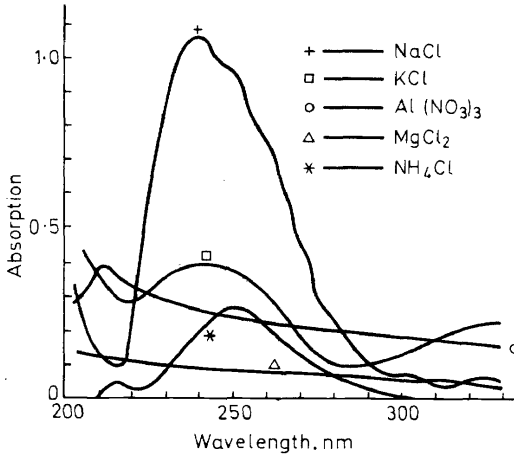


Figure 19. Absorption spectrum of one per cent solutions of chlorides

in an extremely long tube—more than 1 m—was used for practical analytical purposes.

Some examples of molecular absorption are given in *Figures 19, 20 and 21.*

On the other hand refractory elements especially in the matrix of geological samples frequently exhibit a relatively small absorption, probably due to light scattering which cannot be well distinguished from molecular absorption. But this type of background absorption is much smaller even at short wavelengths. For example on the line Pb 217 nm, which we use on a routine

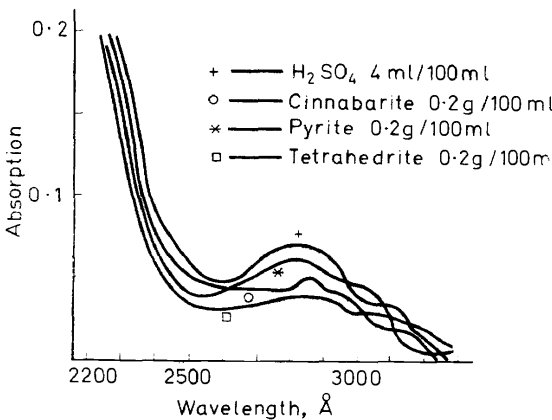


Figure 20. Absorption spectrum of sulphide minerals decomposed by sulphuric acid

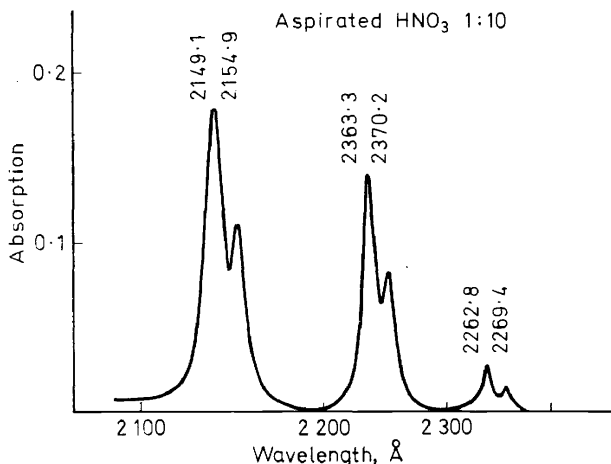


Figure 21. Absorption spectrum of NO

basis for the determination of lead in silicate samples, we can determine tens and even units of p.p.m. (related to the solid sample) directly without any separation or pre-concentration.

The background absorption, however, should be subtracted in every case by measuring the non-specific absorption on some close non-resonant line. Such a correction is based on the assumption that the absorption background may vary only slightly with wavelength. So far we found this assumption not fulfilled in only one case: the determination of bismuth using the line 260.3 nm cannot be carried out in sulphides containing large amounts of antimony, due to the molecular absorption of the antimony polymer in the gaseous state.

Another method, which is better, is described in some papers and in descriptions of new types of atomic absorption instruments (e.g. Perkin-Elmer 403) where the background is corrected by measuring the absorption of a continuous source.

Anyway, all compounds with a high molecular absorption should be removed from the solutions analysed because even if the correction of the background is possible, the analytical error increases. According to our experience the most common such compounds are sulphuric and phosphoric acids and for the region of 225–260 nm also sodium chloride. In general, however, the absorption background does not represent a serious problem when using absorption tubes, compared with other interference effects.

The absorption of the flame with sprayed water is itself usually negligible. At the wavelength of Pb 217 nm and even for the Se 204 nm line the flame absorbs less than two per cent of the signal. At the wavelength of As 197 nm the flame absorption increases markedly and at the wavelength of As 193 nm it is almost impossible to measure, the absorption of the flame being 95 per cent with a very noisy signal.

Memory effect

When absorption cells are used the memory effect must generally be considered. Its mechanism is caused by precipitation of aerosols on to the tube walls from where they are gradually released. The memory effect is therefore—as we have observed—in rough correlation with the volatility of the respective element, but, of course, may depend on various other factors as well, such as the medium of the aspirated solution, temperature of the tube etc. One of the greatest memory effects was observed with tin, which is shown in *Figure 22*.

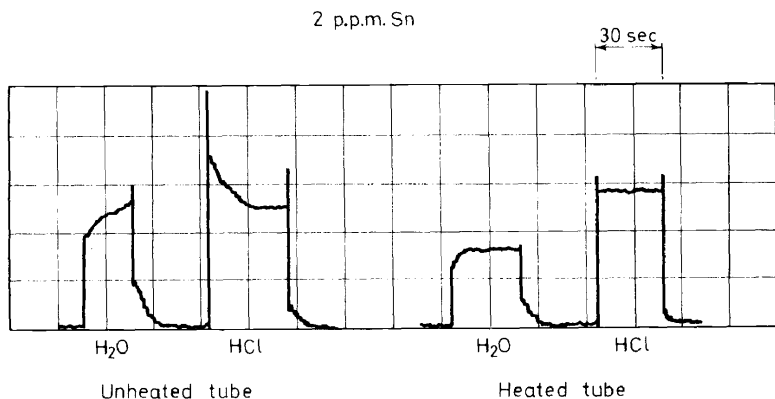


Figure 22. Memory effect with tin

The effect mentioned so far is a result of contamination of tube walls by the element analysed itself. With tin another type of memory effect was also observed. When a pure tin solution was aspirated after a sample solution with a high concentration of an interferent, e.g. iron, a depression of the tin absorption was found. This confirms that the interference is due purely to reactions in the gaseous state.

In general, the material of the tube should always be considered not only from the point of view of the thermal, mechanical and chemical resistance—which are obvious—but also with regard to the possible contamination of the element under test, which could perhaps make the determination impossible. In our laboratory we found this when using ceramic tubes for the determination of copper, and when we tried tubes contaminated by lead after the analysis of galena for lead determinations in other minerals.

In the course of routine analyses when sufficient care is given to properly cleaning the device after every two or more measurements by means of aspirating pure solvent or diluted hydrochloric acid for some seconds no such effects that would negatively affect the analytical results were observed.

Detection limit

In all our work so far we have considered the sensitivity of the respective determinations which is defined as the concentration that produces one per cent absorption. This value gives the possibility for estimation of the

particular element with the particular device. If we compare the detection limits (defined as the concentration that produces absorption equivalent to twice the magnitude of the fluctuation in zero absorption), then the light

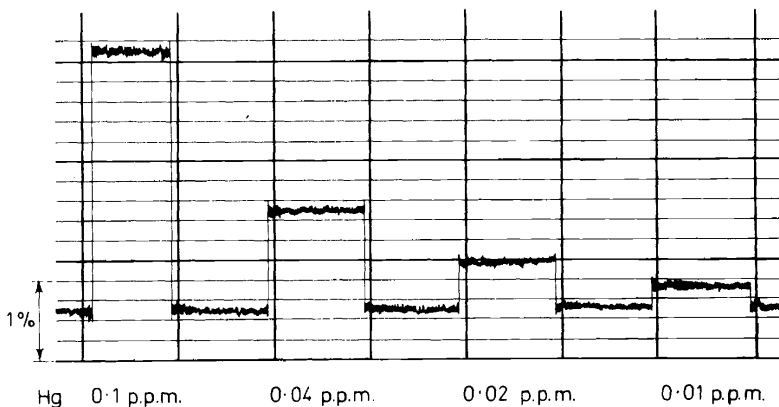


Figure 23. Detection limit of mercury

source and the overall stability of the instrument are the two decisive factors. The detection limit is, however, a value defining also the stability of the absorption medium and therefore it is of importance when characterizing the absorption tube technique. Unfortunately, it is very difficult to separate the noise of the absorption medium from the noise of the rest of the instrument which in our case was not the best. In Figure 23 you can see an example of mercury which has a relatively stable source of radiation (discharge lamp). In this case, the detection limit is 0.006 to 0.008 p.p.m. which is about four times lower than the sensitivity.

APPLICATIONS AND PROSPECTS

In the chemical laboratory of the Geological Survey of Czechoslovakia absorption tubes are used for routine analyses for a number of trace metals. The choice of our methods is controlled chiefly by the wishes of geologists and geochemists who are not—perhaps fortunately—interested in the determination of all elements which we are able to isolate.

Most elements that are determined occur in sulphide minerals. For their decomposition we use a dissolution in acids and directly measure Ag, Pb, Cd, Bi, Mn, Sb in the acid solutions (while Zn and Cu are determined with a Perkin-Elmer 303). We always use the analytical curve method, the standard solutions being in the medium of the acid mixture chosen for the respective element, i.e. for silver, nitric plus tartaric acids, and hydrochloric plus tartaric acids for the others. Only for manganese determination in galenas is the matrix in standard solutions adjusted by addition of lead. Due to many interference effects the tin determination is the only one we perform after chemical separation by electroanalytical deposition.

Lead in silicates is directly determined after decomposition of the samples

by perchloric plus hydrofluoric acids, and tin after the electroanalytical separation. The results of the determination of lead and tin are shown as an example in *Table 5*.

Table 5. Results of determination of lead and tin

Sample	% Pb found by		Sample	% Sn found by	
	AA	X-ray		AA	Polarography
Sandstone 1	0.0027	0.0026	Spilite	0.00023	0.00025
Sandstone 2	0.0012	0.0010	Granite 1	0.00045	0.0005
Claystone	0.0054	0.0050	Shale	0.00045	0.0005
Shale	0.0073	0.0060	Granite 2	0.084	0.09
Sandstone 3	0.0022	0.0020	Granite 3	0.0094	0.010
Sandstone 4	0.0028	0.0026	Granite 4	0.023	0.028
G-1	0.0050	0.0050	Granite 5	0.059	0.06
W-1	0.0009	—	Greisene	0.16	0.16

The methods mentioned, however, are not the only ones possible and further analytical procedures may be developed.

In my opinion, the absorption cell technique is one of the promising modifications of atomic absorption spectrometry. The absorption cell technique improves the sensitivity considerably and generally also the detection limits. In addition it enables us to study some special problems of interferences, atomizing mechanisms etc. Another prospective use is the study of molecular absorption in the gaseous state.

From the point of view of practical analytical problems the sensitivity improvement often allows direct and thus rapid and simple determinations of trace elements. And if we have been successful in analysing complicated geological samples which may be considered perhaps as some of the most difficult materials for analysis, it can be taken for granted that application for other types of material is also possible.

I hope this technique will be further developed in the future and that perhaps some new devices, especially with non-flame sampling, will prove to be even more effective. To date, only the prolonged optical path is generally considered. The advantage of shielding the flame from the external atmosphere will, I believe, prove equally advantageous. I hope that future authors will be patient enough to exploit all the possibilities hidden in the absorption tube technique.

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