THE EMISSION SPECTROSCOPY OF SOME ELEMENTS IN HIGH-TEMPERATURE FLAMES

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The emission of atoms of a large number of elements in laminar high-temperature acetylene–N_2O, H_2–N_2O, H_2–O_2, acetylene–air, and H_2–air flames was studied; of these the most suitable are flame mixtures containing N_2O. Methods were developed for determining Ca, Sr, Ba, for Cu, Cr, Mn and Ni in steels and for Cu, Fe, Mn and Ni in aluminium alloys using an acetylene–N_2O flame. A small chemical interference for the matrix elements was found provided that a mono-chromator with good resolution and with a small amount of scattered light was employed. These conditions are fulfilled by most modern atomic absorption instruments with which comparable results are obtained.

The effect of accompanying elements and more complicated matrices is far less pronounced with emission spectroscopy employing high-temperature flames than with atomic absorption spectrometry. In addition, the dependences of the emission intensity on the element concentration are measurable over a much wider concentration range. Primary irradiation sources are not required and commercial instruments can be used simultaneously for atomic absorption spectrometry and for the emission technique. In general, laminar flames are employed using gas mixtures with fuel premixing, as turbulent flames with direct injection of the solution exhibit much poorer short-time and prolonged signal stability in spite of their more effective sample nebulization and simple applicability for any gas mixture. Koirtyohann and Pickett[1] described the emission of atoms of alkaline earth elements in acetylene–nitrous oxide flames; Fassel and Becker[2] used premixed acetylene–oxygen–nitrogen or acetylene–nitrous oxide flames. The flame emission determination of alloying elements in steels was recommended by Fassel, Slack and Kniseley[3] who also mentioned that the analytical sample and alloy standard need not have identical compositions.

   This work deals with the emission of a larger number of elements on an apparatus constructed in our laboratory using four fuel mixtures, primarily acetylene–nitrous oxide and hydrogen–nitrous oxide and establishes the conditions for determining calcium, strontium, barium and of some alloying additives in low-alloy steels and aluminium alloys. It was demonstrated that elements can be reliably determined in high temperature flames by the emission method and that for some elements the parameters are better than those corresponding to determination by atomic absorption spectrometry. The greatest advantage lies in considerable elimination of the chemical interference by the sample matrix. In contrast, the danger of spectral interference by lines and molecular bands of the sample matrix is greater. The emission

method is not dependent on the availability of suitable hollow-cathodes lamps. It requires, however, a monochromator with good resolution and a low scattered light level.

EXPERIMENTAL AND RESULTS

Standard solutions of ions of calcium, strontium, barium, copper, manganese and iron were prepared by dissolving $Ca(NO_3)_2.4 H_2O$, $SrCl_2.2 H_2O$, $BaCl_2.2 H_2O$, $CuCl_2.2 H_2O$, $Mn(NO_3)_2$. .6 H_2O and $Fe(NO_3)_2.9 H_2O$ in doubly distilled water, which was acidified if necessary with concentrated nitric acid, so that the concentration of the element was 1 mg/ml; the solutions were standardized gravimetrically or by EDTA titration. The initial salt solutions for studying interferences contained 10 mg of the element per ml. The stock solution for suppressing ioniza- tion of the atoms contained 100 mg KCl per ml. All the chemicals employed were *p.a.* purity. The content of the inorganic impurities in these chemicals was controlled by emission spectral analysis. The standard iron solution was prepared by dissolving 2·5000 g of spectral pure iron in 50 ml HCl (1 : 1) with addition of a few drops of concentrated HNO_3 and diluting with doubly distilled water to 500 ml. The standard aluminium solution was prepared by dissolving 13·903 g of $Al(NO_3)_3.9 H_2O$ in 500 ml of doubly distilled water and acidified with a few drops of concen- trated HNO_3. The content of both elements was 10 mg element in 1 ml. Standard solutions of low- -alloy steels were prepared from standard steel samples Nos 162—171, ČKD Research Institute Prague, containing 0·035—0·65% copper, 0·015—2·82% chromium, 0·025—1·63% manganese and 0·025—2·77% nickel.

Procedure: 2·500 g steel were dissolved in 50 ml boiling HCl (1 : 1) and the insoluble residue was dissolved in a few drops of concentrated HNO_3. Nitrogen oxides were removed by brief boiling and the solution was diluted to 500 ml with distilled water.

The standard aluminium alloy solutions were prepared from standard Zh 21—24 ČKD research Institute samples containing 0·11—1·08% copper, 0·09—0·9% iron, 0·08—0·98% manganese and 0·065—1·3% nickel.

Procedure: 0·2000 g of aluminium alloy sample were dissolved slowly in a mixture of 1 ml HNO_3 (1 : 10) and 25 ml HCl (1 : 10). The solution was diluted to 200 ml with distilled water. Further standard samples were obtained by double dilution of Zh 21—24 standard in a ratio of 1 : 1 with a 1 mg/ml aluminium solution.

The emission flame spectrometer was constructed from a standard single slit burner with $l = 5$ cm and a Unicam diffusion atomizer for atomic absorption spectrometer SP 90, quartz lenses with $f = 80$ mm and diameter 35 mm, an Elpho, Zeiss synchronous chopper with chopping frequency 62 Hz, an SPM 2 Zeiss monochromator with a 651 lines/mm grating, reflection at 550 nm, with dimensions 70 × 65 mm; in some cases a Si 68 prism was used. In addition, photo- multiplier M 12 FVC 52A Zeiss with a PHO 1 Zeiss high-voltage source, Unipan selective nano- voltmeter, type 237 (Poland) and a Zeiss B1T1 recorder were employed.

A specially constructed burner with fuel premix[4] was employed for acetylene-air and hydro- gen–oxygen gas mixtures.

The flame spectral background was recorded on a B1T1 recorder combined with a monochro- mator a wavelength range of 250—600 nm. For acetylene-air, acetylene–oxygen, hydrogen–air and hydrogen–oxygen flames, the characteristic inner, primary zones with kinetic combustion predominating and the outer secondary zones with diffuse combustion were employed.

The detection limit was calculated for $3s_B$ where s_B is the standard deviation of the background according to the relationsip

$$\text{d.l. (ppm)} = \frac{c}{\text{emission intensity}} \cdot 3s_B .$$

The emission intensity is expressed in terms of the voltage indicated on the selective nanovoltmeter.

The determined detection limit has only relative significance for comparison of methods on one apparatus. It generally depends primarily on the intensity of the particular spectral line, degree of atomization, ionization and autoabsorption and is influenced by the characteristics of the atomization system, the solvent employed, the stoichiometry of the gases in the mixture, the position in the flame employed during the measurement, the level and variability of the noise and the time constant of the measuring apparatus.

Each point on the calibration curve was measured three times and the background was found five times in each case. The precision of the emission measurement depends primarily on the stability of the flow of fuel and oxidant, on the precision of the adjustment of the monochromator lines and on precise determination of the sample background.

In work connected with concentrated sample solutions it is necessary to carefully wash the burner with distilled water, as apparently negligible contamination of the burner results in a change of the measuring parameters and thus in a decrease of the precision.

The flame temperature was measured with the described apparatus using the two line atomic absorption method and employing a continuous radiation source (W-lamp, 12 V, 30 W) and indium as a thermometric element[5].

At low absorbances, $A < 0.3$, the relationship for the absolute temperature was employed

$$T\,(\text{K}) = \frac{E_1 - E_0}{k. \ln\left(\dfrac{g_1 f_1}{g_0 f_0}\right)\left(\dfrac{\lambda_1}{\lambda_0}\right)\left(\dfrac{A_0}{A_1}\right)},$$

where A_0, A_1 are the absorbances at wavelengths λ_0, λ_1, g_0, g_1 are the statistical weights of energy levels E_0 and E_1. The measured ratio A_0/A_1 is dependent only on the temperature and not on the spacial distribution of the atoms if the flame is in excitation equilibrium.

Relative values of g.f and energy levels with an error of $\pm 3\%$ for indium[6] are:

nm	g.f	E, cm^{-1}	
		lower level	higher level
410·18	0·288	0	24 373
451·13	0·628	2 213	24 373

The relationship for the absolute temperature in measurements employing indium is

$$T\,(\text{K}) = \frac{3146}{\ln\,[2\cdot637(A_0/A_1)]}.$$

Indium is useful as a thermometric element at temperatures of $1220-3500$ K. At small absorbance values ($A \sim 0.03$) the measuring error is about $\pm 5\%$ relative (~ 20 K) at low temperatures and $\pm 10\%$ for high temperature flames. The signal for nebulized water ($T = 100\%$), the signal with closed slit ($T = 0\%$) and the signal for nebulization of an indium solution (5 and 10 mg/ml In) were measured in each case. The absorbances were calculated or determined graphically. This method is very useful for measuring flame temperatures; however, it requires

a monochromator with high dispersion and it must be possible to reproduce its adjustment so that the value scatter is sufficiently small.

A Survey of Laminar Flames with Pre-Mixed Fuels

a) *Hydrogen–air*: At low fuel flow-rates this flame is transparent and invisible; at higher hydrogen flow-rates the primary combustion zone is pinkish and transparent and the secondary zone is light blue. Even when there is a marked fuel excess, the flame is not reducing. The flame spectrum has a very low background level. In the primary zone OH emits in the region 306—320 nm; in the secondary zone a low intensity band at 280—300 nm was recorded.

b) *Hydrogen–oxygen*: The primary tone of this flame is bluish white; the secondary zone is light blue and almost transparent. In fuel-rich flames the size of both zones increases and their clarity is decreased. At ratios of $\varrho =$ oxidant/fuel $= 0.1$, the flame is invisible. Here the spectrum of the primary combustion zone also has a low background level, only the OH band as 280 to 320 nm is present and is more intense in the secondary zone.

Optimal conditions for emission of metal atoms are at $\varrho = 0.3 - 0.25$ at $0.25 - 1.0$ cm above the burner edge[7].

c) *Acetylene–air*: The primary combustion zone is transparent and light blue. Its spectrum was found to contain emission by OH (280—360 nm), CH (390 and 431 nm), CN (387, 388, 418, 419, 421, 586 nm) and C_2 (474, 517, 554 nm).

The secondary combustion zone is yellow, with a yellow-white edge, with weaker background and less intense emission by OH, CN and C_2. Emission by C_3 was not identified in the flame.

d) *Acetylene–nitrous oxide*: The primary combustion zone is separated from the secondary post-reaction zone by a typical red interconical zone. Its size depends on the ratio of oxidant and fuel. The flame background in the interconical zone is particularly intense and consists of the CN (387, 388, 418, 419, 421 and 586 nm), NO (227, 236, 259 nm), C_2 (474, 517, 554, 564, 584, 633, 648, 663 nm), C_3 (405 nm), NH (336, 343, 348 nm), CH (390, 431 nm) and OH (306 nm) bands. The intensity of various maxima in the flame spectrum depends on the stoichiometry of the gas mixture. With decreasing ϱ, the emission of NH, CH and C_2 decreases and the OH maximum increases.

Flames with $\varrho = 2 - 3$ are most useful for atomization of elements with a tendency to form thermostable monooxides. The formation of stable monooxides is severely limited in flames with this gas mixture, because the concentration of free carbon radicals in the primary and in the interconical zone is several orders higher than that corresponding to thermal equilibrium.

e) *Acetylene–oxygen*: The flame spectrum is more intense than for acetylene–air mixtures. The primary zone has a less intense region at 280—300 nm and a more intense region containing the OH emission band at 306—330 nm. From 360 mm the continuous spectral background increases and emission by CH, C_2, CO and CN appears. The spectral background in the secondary combustion zone is simpler. The bands of CH, CN and C_2 were not identified here.

f) *Hydrogen–nitrous oxide*: The flame is stable for a broad range of fuel flow-rates at a constant N_2O flow. In contrast to the literature data[8], a much lower combustion rate, at most 40 cm s^{-1}, was found for the same type of burner. The flame temperature rapidly decreases vertically above the primary combustion zone. A fuel-rich flame and emission measurement $0.2 - 0.4$ cm above the primary combustion zone are optimum. The primary combustion zone is yellow-white, at higher hydrogen flow-rates it becomes a transparent blue with yellow edges.

The secondary combustion zone is light blue and almost transparent. The interconical zone has a weak background consisting of OH bands (280—330 nm) and very weak NO (236, 259 nm) and NH (336, 343, 348 nm) emission.

The temperatures of laminar flames with given stoichiometry were measured by the described atomic absorption method and are compared with the literature data in Table 1.

Emission of Potassium, Calcium, Copper, Manganese and Iron Atoms in Various Flames

The behaviour of the model elements was studied in the concentration range 1 to 100 μg/ml in H_2-air, H_2-O_2, acetylene-air, H_2-N_2O and acetylene-N_2O flames using the described burners with nebulization of pure aqueous solutions of the salts of the elements at wavelengths of K 776 nm, Ca 422·67 nm, Cu 324·75 nm, Mn 403·07 nm and Fe 371·99 nm. The parameters for determination of these elements in various flames and at optimum stoichiometry of the gas mixtures are given in Table II. The sensitivity and detection limit are clearly dependent both on the fuel mixture employed and on its stoichiometry with the nebulizer and burner type employed.

In spite of their high temperatures, flames of mixtures of hydrogen with oxygen and nitrous oxide are apparently not suitable for determining elements forming stable oxides (Al, Ba, *etc.*). The only advantage of these flames is the lower background level. In acetylene-oxygen flames the sensitivity and detection limit of most elements are also generally an order lower than for acetylene-nitrous oxide flames and are comparable with data for acetylene-air flames.

In comparison of N_2O and H_2 or CH_2 flame mixtures, of the common elements only Cu, Fe, Cd, K and Na have similar detection limits; otherwise this limit and determination sensitivity are much lower in flames employing hydrogen. In spite of the relatively high temperature of this flame, some elements are not atomized effectively

TABLE I

The Temperatures of Laminar Flames of Some Premixed Gas Mixtures

Flame	Fuel	Oxidant	Temperature, K		Ref.
			measured	literature	
H_2-air	2·5	5·5	1 830[a]	2 000	9
C_2H_2-air	1·2	5·5	2 460[a]	2 450	9
				2 410	10
C_2H_2-N_2O	4·0	5·5	3 080[b]	2 950	9
				2 880—3 100	11
H_2-N_2O	4·0	5·0	2 540[a]	2 900	9

[a] Secondary flame zone; [b] interconical zone.

and are readily converted to stable monooxides in the dry aerosol. The relative decrease in the chemical interference, as is common with low-temperature flames, such as the effect of aluminium and phosphorus on the determination of calcium, etc.[2,12] is useful. An acetylene–nitrous oxide flame is most useful for the determination of most elements in spite of the relatively high flame background. The measurement of the emission in flames with gas mixtures with N_2O is also useful as most commercial

TABLE II

Parameters for Determining Selected Elements for Several Types of Laminar Flames
    The values given were found without suppression of ionization.

Flame	Detection limit ppm	Sensitivity μV/ppm	Linear up to ppm
C_2H_2—N_2O	0·50	8·5	88
H_2—N_2O	0·30	28·9	65
H_2—O_2	0·48	18·4	50
C_2H_2—air	0·043	5·8	40
H_2—air	0·026	18·4	50
C_2H_2—N_2O	0·0014	36·3	30
H_2—N_2O	0·016	46·2	32
H_2—O_2	0·060	1·3	80
C_2H_2—air	0·009	1·7	95
H_2—air	0·036	1·1	110
C_2H_2—N_2O	0·014	109·7	39
H_2—N_2O	0·050	49·6	35
H_2—O_2	0·42	4·1	100
C_2H_2—air	0·11	2·4	130
H_2—air	1·6	0·9	180
C_2H_2—N_2O	0·10	26·6	21
H_2—N_2O	0·15	10·6	83
H_2—O_2	3·4	1·8	110
C_2H_2—air	0·40	0·9	165
H_2—air	2·0	0·3	290
C_2H_2—N_2O	0·60	31·7	25
H_2—N_2O	0·75	3·6	180
H_2—O_2	3·5	0·5	900
C_2H_2—air	0·83	0·4	920
H_2—air	2·8	0·2	850

atomic absorption spectrometers can be used, along with the burners and nebulizers. Potassium salts were employed as recommended[13] for decreasing the atom ionization. Mineral acids lead to a special type of interference, which increases the emission signal at low concentrations and decreases it at higher concentrations[14].

The Determination of Ca, Sr and Ba in C_2H_2–N_2O and H_2–N_2O Flames

Calcium: The optimum procedure for the Ca resonance line at 422·67 nm involved flow-rates of 3·6 l min^{-1} C_2H_2 and 5·5 l min^{-1} N_2O with a red interconical zone 6 mm high and 3·8 l min^{-1} H_2 and 5 l min^{-1} N_2O. Calcium ionization is suppressed by the presence of a potassium salt in solution. The calcium emission increases with increasing potassium concentration and is constant from 500 µg K/ml. In the presence of 1 mg K/ml the intensity of the Ca emission in C_2H_2–N_2O flames increases over the whole concentration range in H_2–N_2O flames, especially up to 2 µg Ca/ml. In both flames the dependence of the emission intensity on the Ca concentration is linear up to 70 µg/ml; above this concentration autoabsorption begins to become important. The detection limits are 0·08 µg/ml and 0·0014 µg/ml with addition of 1 mg K/ml for C_2H_2–N_2O flames and 0·06 µg/ml and 0·016 µg/ml in the presence of 1 mg K/ml for H_2–N_2O flames. In flames containing acetylene was observed a marked positive effect of a large number of ions for a 10 − 1 000 fold excess of interfering element as a result of suppression of ionization of calcium by the ions of the given element, which confirms the expected effect of elements with ionization potentials up to 7·5 eV (ref.[13]) in the order Zn < Al < Cu < Mg < Ni < Cr < Mn < < Mo < Na. Spectral interference is also caused by the lines of Fe (422·74 nm) and Mo (422·67 nm).

The addition of an optimal amount of potassium (1 mg K/ml) to the solution decreases the chemical interference to a minimum; a 1 000 fold excess of the following elements does not interfere: Na, Mg, Al, Cu, Cr, Ni, Zn, Mn, Fe, Pb, La, Mo, Sr, Ba. The emission of calcium in the presence of potassium is increased practically only by phosphoric acid. A small increase was found with sulphosalicylic acid. The Ca signal and interference from foreign ions is less in H_2–N_2O flames, La ≪ Cu < Ni, Pb < Na ≪ Cr < Mn. In some cases a negative effect on the emission was observed (aluminium). Organic hydroxo acids, NO_3^-, 5-sulphosalicylic acid and acetic acid have only a small effect on the Ca emission up to a concentration of 0·1M; phosphoric acid also increases the emission here. In the presence of potassium (1 mg K/ml) even a 1 000 fold excess of common elements has no effect. A slight increase in the signal was observed in the presence of phosphoric acid.

Strontium: With the optimum stoichiometric mixture of C_2H_2, 3·61 . min^{-1}, and 5·5 l . min^{-1} N_2O and the Sr line at 460·73 nm, the dependence of the emission on the concentration is linear up to 10 µg Sr/ml using a parallel burner and up to 400 µg Sr/ml using a crossed burner. The dependence of the signal magnitude on the potas-

sium content increases to 500 µg K/ml; in subsequent measurements 1 mg K/ml was employed to suppress ionization. The detection limit is 0·008 µg Sr/ml and 0·0023 µg Sr/ml in the presence of 1 mg K/ml.

In the absence of potassium, Na, V, Cu, Zn, Al, Fe, La, Mo, mineral acids up to 0·05M including phosphoric acid and sulphosalicylic acid up to 0·1M strongly increase the strontium emission; acetic acid up to 0·1M does not interfere. In the presence of potassium, practically only vanadium increases the emission because of spectral coincidence with the VO band (460·73 nm); the emission decreases markedly in the presence of aluminium ($c_{Al}/c_{Sr} = 1000$).

At optimum stoichiometry of the H_2 (3·9 l . min^{-1})–N_2O (5·1 l . min^{-1}) mixture the intensity of the emission is linearly dependent on the Sr concentration up to 100 µg Sr/ml using a parallel burner. At higher concentrations autoabsorption occurs. Potassium has a less marked effect and is most useful at low concentrations up to 10 µg Sr/ml. The detection limit is 0·15 µg Sr/ml and 0·013 µg/ml Sr in the presence of 1 mg K/ml. The presence of Na, Ni, Mn, La, Mo, *etc.* increases the strontium emission markedly; the emission decreases in the presence of Al from the ratio $c_{Al}/c_{Sr} = 10$. Among the mineral acids, only phosphoric acid up to 0·05M increases the emission markedly, as do sulphosalicylic and acetic acid at concentrations of 0·1M. In the presence of 1 mg K/ml in solution, only a ten-fold excess of Al has a negative effect and a 1 000 fold excess of Si, V, Na and Mo increases the emission.

Barium: The maximum emission was attained for the atomic resonance line of Ba at 553·55 nm. The emission of the ionic lines at 544·4 nm and 493·4 nm was weak and frequently markedly dependent on the concentration of further ions in the solution. For optimum stoichiometry of the C_2H_2 (3·6 l . min^{-1})–N_2O (5·5 l . min^{-1}) mixture, the intensity of the emission is linearly dependent on the Ba concentration up to 200 µg/ml; autoabsorption occurs at higher concentrations. In the presence of an optimal concentration of potassium (5 mg K/ml), the emission intensity increases markedly; the concentration dependence is linear up to 50 µg Ba/ml or 400 µg Ba/ml using a crossed burner. The detection limit is 0·01 µg Ba/ml and 0·003 µg Ba/ml in the presence of 5 mg K/ml.

The emission of pure Ba solutions is increased by Na, Ca, Mg, Sr, La, Cu, Mn, and V from $c_M/c_{Ba} = 1$. With Ca, La, Mg, Sr and V simultaneous spectral interference occurs with the lines or bands of CaOH 554 nm, LaO 553·55 nm, MgO 553·55 nm, Sr 553·48 nm and VO 553·58 nm. In the presence of 5 mg K/ml, the positive effect of Mn, Cu and Na ions is small. Ca and V interfere strongly only when present in thousand-fold, Mg and La in hundred-fold and Sr in ten-fold excess. Mineral acids and citric acid decrease the Ba emission from 1M concentration in the presence of 5 mg K/ml, probably as a result of the increased viscosity of the solution; sulphosalicylic acid increases the emission up to 0·5M concentration.

When using a flame with H_2 3·9 l . min^{-1} and N_2O 5 l . min^{-1}, the intensity of

the Ba emission is linearly dependent on the concentration in the range $2-400$ µg Ba/ml. At concentrations below 2 µg Ba/ml, primarily BaOH is formed and the ionization of Ba is increased; thus low concentrations cannot be measured without addition of K. The emission intensity is increased markedly in the presence of 5 mg K/ml and it is linear up to 400 µg Ba/ml. The detection limit is 1·6 µg Ba/ml and 0·0065 µg Ba/ml in the presence of 5 mg K/ml. The Ba emission is affected by foreign ions even in the presence of 5 mg K/ml; Ca interferes from a ratio of $c_{ca}/c_{Ba} = 1$ through formation of CaOH and Sr and V interfere above a 100-fold excess.

Determination of Copper, Chromium, Manganese and Nickel in Steels

The most intense lines with optimum signal/background ratios were chosen for the determination: Cu 324·75 nm, Cr 425·43 nm, Mn 403·07 nm, Ni 351·50 nm. Using an SPM 2 monochromator, these lines are not disturbed by any component found in steels.

The emission of Cu, Mn and Ni decreases with increased fuel flow-rates; the emission of Cr increases. Consequently, the emission of Cu, Mn and Ni was measured using a fuel-poor flame, optically characterized by a 3 mm red zone in C_2H_2–N_2O flames and an intense 2 mm yellow-white zone in H_2–N_2O flames. The chromium emission was measured with a fuel-rich flame with a 10 mm red zone or a hydrogen flame with a 5 mm zone. Optimum gas flow-rates for Cu, Mn and Ni are 3·0 l . min^{-1} C_2H_2 and 5·5 l . min^{-1} N_2O or 3·0 l . min^{-1} H_2 and 5·0 l . min^{-1} N_2O, and for chromium 3·8 l . min^{-1} C_2H_2 and 5·5 l . min^{-1} N_2O or 4·4 l . min^{-1} H_2 and 5·0 l . min^{-1} N_2O.

The presence of potassium markedly increases the emission of chromium and manganese, but has only a slight effect on the emission of copper and nickel. In ensuing experiments 5 mg K/ml as KCl was employed. The presence of 5 mg Fe/ml as ferric chloride in pure solutions of the determined elements has no effect on the concentration dependence of the emission of these elements.

For both flame types the calibration dependence of solutions of standard samples containing $0·035-0·65\%$ Cu, $0·015-2·82\%$ Cr, $0·025-1·63\%$ Mn, $0·025-2·77\%$ Ni were measured. The calibration curves for copper and manganese have similar slopes for both flames; the sensitivity of the determination for nickel and chromium in the H_2–N_2O flame is much lower.

During nebulization of each sample, the background for water and for a standard iron solution was measured. After measuring each steel sample and iron solution it is recommended that distilled water be nebulized to prevent clogging of the burner and to increase the precision of the determination.

Copper and manganese can be determined with both flame types; nickel can be determined with a hydrogen flame only for contents above 0·25%. Chromium can be

determined only using acetylene flames. The detection limit and relative error for five measurements of the standard with the lowest content of the particular element are given in Table III.

The Determination of Cu, Fe, Mn and Ni in Aluminium Alloys

Up to 5 mg Al/ml, aluminium does not measurably affect the emission of Cu at 324·75 nm, Fe at 371·99 nm, Mn at 403·07 nm and Ni at 351·50 nm and none of these lines coincide with the aluminium lines. The potassium content only slightly increases the emission of Cu, Fe, Mn and Ni in pure solutions; in the presence of aluminium it has a negligible effect. The aluminium content here is apparently sufficient to decrease ionization and the potassium has no effect.

The dependence of the emission of Cu, Mn and Ni on the fuel flow-rates was the same as that for these elements in iron samples. A fuel-poor flame was used for deter-

TABLE III

Determination of Additives in Steels and in Aluminium Alloys
A C_2H_2—N_2O flame; B H_2—N_2O flame.

Element	Flame	Linear calibration curve range	$s_x \cdot 100/\bar{x}$	Detection limit
		% steels	%	% sample
Cu	A	0·01 — 1·4	+1·6	0·002
	B	0·02 — 1·9	+5·3	0·003
Cr	A	0·01 — 4·2	+1·1	0·0014
	B	0·08 —10·0	−6·2	0·01
Mn	A	0·01 — 2·0	+2·0	0·0021
	B	0·01 — 2·5	+0·8	0·0016
Ni	A	0·007— 6·5	+0·7	0·0011
	B	0·02 —12·0	−2·3	0·0033
		aluminium alloys		
Cu	A	0·01 —1·5	+1·5	0·002
	B	0·015—2·0	+4·1	0·003
Fe	A	0·1 —1·8	−2·6	0·03
	B	0·2 —3·0	−3·9	0·086
Mn	A	0·006—2·0	+0·4	0·001
	B	0·006—3·0	−2·5	0·001
Ni	A	0·001—2·6	+0·1	0·0003
	B	0·02 —5·5	+0·15	0·009

mining iron in aluminium: $3 \, l \cdot min^{-1}$ C_2H_2, $5 \cdot 5 \, l \cdot min^{-1}$ N_2O or $3 \, l \cdot min^{-1}$ H_2 and $5 \, l \cdot min^{-1} N_2O$.

The calibration curve for sample solutions with $0 \cdot 11 - 1 \cdot 08\%$ Cu, $0 \cdot 09 - 0 \cdot 9\%$ Fe, $0 \cdot 08 - 0 \cdot 98\%$ Mn and $0 \cdot 065 - 1 \cdot 3\%$ Ni are almost linear for both flame types. Because of a lack of standard aluminium alloy samples, these solutions were diluted in a ratio of $1 : 1$ with pure aluminium solution with a concentration of 5 mg Al/ml. The background values obtained by nebulization of distilled water and of a standard aluminium solution containing 5 mg Al/ml were identical. The manganese emission in both flame types has identical intensity for the same concentrations; the emission of iron and nickel in hydrogen flames under identical conditions is much lower and the slope of the calibration curve decreases markedly.

The detection limit and relative error for 5 measurements for a standard with the lowest content of the given element are given in Table III.

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