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Determination of Trace Elements in Oils by Plasma Emission Spectroscopy

A.J. DIJKSTRA and **D. MEERT**, N.V. Safinco, Research and Development,
Prins Albertlaan 13, B-8700 Izegem, Belgium

ABSTRACT

An analytical method for the determination of phosphorus and other elements at low concentrations in edible oils has been developed using a plasma emission spectrometer. The method is fast because it eliminates the ashing process in sample preparation and because the actual measurement takes less than 1 min. Reproducibility and accuracy of the measurement are good and very low detection limits have been observed, e.g., 0.5 ppm for phosphorus and 5 ppb for copper. However, the long-term stability of the instrument cannot as yet be guaranteed and a procedure that prescribes regular measurement of samples of known concentration is essential as a means of detecting any drift in the output signal.

INTRODUCTION

A rapid and accurate analysis of the phosphorus content of edible oils constitutes a desirable tool in oil refining. Metals, particularly copper and iron, seriously affect oil quality, or in the case of lead, arsenic and mercury, may be the subject of food legislation, which again calls for analytical methods.

Consequently, a number of analytical methods have been developed and adopted as official methods. These methods have in common that the elements to be determined are first of all concentrated by ashing, or by volatilization, in the case of mercury. Ashing, however, can lead to losses and/or contamination. Improved procedures have been proposed (1), but duplicate analyses still are a necessary precaution. Besides, the ashing process takes up to 9 hr (1) which is often too long for effective process and quality control.

Naturally, other methods have been investigated since novel instruments became available. Flame atomic absorption (2,3) still requires ashing of the sample but carbon rod flameless atomic absorption spectroscopy (4) obviates ashing. Finally, the use of a graphite furnace in flameless atomic absorption spectroscopy was developed for the determination of trace elements in oil (5), which was found to be a further improvement.

When it was reported (6) that the addition of a lanthanum salt to an aqueous solution of a phosphorus compound not only increased the phosphorus signal but probably also minimized the sensitivity difference between various phosphorus compounds, this finding was extended to edible oils (7,8). Apparently necessary improvements have been reported (9) recently, in that the use of an organic lanthanum salt (lanthanum-2,4-pentadionate) dramatically improved the reproducibility as well as the sensitivity. Using sample volumes of 20 μL and photodiode temperature control, a reproducibility of 2% at levels above 20 ppm P is reported with a detection limit of 0.5 ppm P.

Some authors (5,7) mention smoke formation in the graphite furnace as a drawback particular to edible oils. The use of a higher pyrolysis temperature as provided by a plasma solves this problem. Accordingly, plasma emission spectroscopy has been evaluated as a fast analytical method for trace amounts of phosphorus and other elements in edible oils.

The method analyzes the oil as such and thus obviates ashing and its inherent risks of spurious results. The fact that the method to be described requires a much larger sample volume than methods employing atomic absorption spectrometry is not regarded as a serious disadvantage in an industrial environment where speed, reproducibility and low detection limits as provided by plasma emission spectroscopy are essential.

EXPERIMENTAL PROCEDURES

Equipment

A recent survey of plasma emission spectrophotometry equipment (10) and their emission sources, in particular, codetermined the choice of instrument used in this investigation: Spectraspan IV (Spectrametrics Inc.) coupled with an electronic data terminal (Texas Instruments, Model 743 KSR).

In this instrument, a DC argon plasma arc is generated between 2 carbon anodes and a tungsten cathode at a current of 7.5 A at 40 V. The arc has the shape of an inverted Y into which the sample is fed as an aerosol from below. The sample itself is fed by means of a peristaltic pump at a fixed rate of 1.6 mL/min to a nebulizer where about 20% of the sample is introduced into an argon stream as an aerosol; the fraction of the sample that is not nebulized is removed from the nebulizer by the same peristaltic pump. Collection of this fraction permits the nebulizer efficiency to be determined.

At the junction of the plasma the sample is introduced into the 6,000-7,000 K excitation region where the sample molecules are thermally dissociated and the resulting atoms are excited. In case of organic samples, part of the sample burns outside the plasma arc, thus leading to some smoke and fumes. It is therefore necessary to install a hood and exhaust fan which also prevents ozone formed in the plasma from fouling the laboratory atmosphere.

The light emitted from the excitation region is focused onto an input slit and subsequently dispersed by means of an echelle grating and a double pass quartz prism thus leading to an X-Y dispersion pattern that can be recorded photographically for a qualitative multi-element analysis. In case of a quantitative single-element analysis, the position of the grating and the prism are adjusted to direct the light of the appropriate wavelength through the output slit onto a photomultiplier tube.

The equipment is provided with a simple, preprogrammed microprocessor. It performs the following functions: (a) automatically chooses the optimal amplifier gain; (b) stores and allocates values for high and low standards; (c) calculates concentrations in samples by linear interpolation; (d) calculates average and standard deviation of replicate measurements; (e) assigns samples sequential numbers; and (f) signals some abnormalities through coded status messages.

Operating Procedure

Operating the Spectraspan IV is relatively simple and does not require highly skilled personnel. Once argon flow rates have been set and some manual skill has been acquired in replacing electrodes and their ceramic sleeves and in cleaning the nebulizer and the glass sample tube, operating is a mere push-button affair.

Prior to any determination, the appropriate wavelength must be selected. Thus, a solution of the element to be investigated is nebulized at fairly high concentration and grating, and prism positions are then selected on the basis of maximal signal. Wide input and output slits may be used at this stage.

If necessary, the plasma position may be adjusted at this stage, again on the basis of maximal signal, but in practice, this was found to be almost never necessary. Once the approximate grating and prism positions have been found, the slits to be used during the actual measurements are selected and grating and prism positions are finely adjusted. These instrument set-up procedures take ca. 15 min.

Subsequently, the high standard is fed to the nebulizer and its content of the element under investigation is input to the microprocessor, whereupon the instrument selects the amplifier gain that is optimal for this content in the "autorange" mode of operation. Thereafter, the low standard is fed and input, and the instrument is then ready for a series of measurements.

The duration of single measurements (e.g., 10 sec) and the number of replicate measurements (e.g., 3) can then be chosen as a function of the accuracy required. When a sample is then fed to the instrument and the sample button is pressed, the instrument will automatically record data as illustrated by the following example:

```
TIME = 10   REP = 3   SAMPLE = 15
1  27.8   30.4   29.8   AV   29.3   SD   1.38
1  0044   0907   3968  0000  1013   0991   0999   0997
```

Print-out example:

TIME = 10 : duration of single measurements.
REP = 3 : number of replicate measurements.
SAMPLE = 15 : sequence number of sample.
27.8 30.4 29.8 : calculated concentrations of the individual measurements.
AV 29.3 : average value of calculated concentrations.
SD 1.38 : standard deviation of average value.
0044 : small capacitor is used; gain range 44.
0907 : measured intensity low standard.
3968 : measured intensity high standard.
0000 : concentration input for low standard.
1013 : concentration input for high standard.
0991 0999 0997: measured intensities of the replicate measurements.

In this example, the sample happened to have a concentration that was very low in comparison to the high standard (30 compared to 1,000, where the units used are immaterial).

TABLE I

Analysis of Sunflower Oil Used as Low Standard by Conventional Methods

Lead	<5 ppb
Iron	55 ppb
Copper	10 ppb
Cadmium	1 ppb
Nickel	<5 ppb
Phosphorus	1.1 ppm

Materials

The oils and fats used in this investigation stemmed from routine production; both intermediate stage samples and fully refined samples have been used.

Because the method as just described is not an absolute measurement but is based on an interpolation between a low and a high standard, a calibration is necessary. For this purpose, a fair amount of sunflower oil was set aside and used as low standard. By the addition of known amounts of elements to this oil, high standards were obtained. The oil was analyzed by conventional means (ashing and atomic absorption spectroscopy on the residue) by a specialized laboratory (CIVO-TNO, Zeist, The Netherlands) which reported the results given in Table I. Before these results were known, the low standard was arbitrarily set at 0, which regularly resulted in negative measurement values.

Phosphorus standards were prepared by dissolving triphenylphosphate oil soluble standard for atomic absorption spectroscopy (Merck) in the low standard sunflower oil and by dilution with the same oil.

Nickel and copper standards were prepared from their acetates (Merck) and iron standard from ferric citrate (Merck). The citrate, however, dissolved very slowly in the oil and several days of continuous agitation were required to ensure complete dissolution of the salt.

In the later stages of the investigation Conostan metallo-organic standards (Conostan Div., Continental Oil Co.) were used, both single-element and multi-element standards. The recently introduced Merck standards have not yet been evaluated.

Standards in oil were prepared on a w/w basis. Oil in solvent solutions, on the other hand, were made on a w/v basis. The solvent used was odorless kerosene (Baker) with a boiling range of 200-250 C.

It has been found to be necessary to prepare fresh standards in oil regularly because their concentrations diminish with time. A maximal shelf life of 2 weeks is recommended.

RESULTS AND DISCUSSION

Choice of Solvent

Early experiments showed that feeding undiluted oil to the nebulizer did not result in a proper aerosol and led to larger differences between repeat measurements than had been observed for aqueous solutions. Lowering the oil viscosity by heating the oil to 40 C gave some improvement so that it was decided to lower the viscosity even further by diluting the oil sample with a solvent. Such a dilution lowers the concentration of the element to be analyzed and thus results in a loss in sensitivity. In practice, however, this loss in sensitivity was more than offset by the gain in sensitivity resulting from improved reproducibility due to greater aerosol stability.

Several solvents were tried. Low-boiling-point (bp) solvents (chloroform, diethyl ether) evaporated inside the nebulizer, thus causing fluctuations in the aerosol flow rate. Ketones (acetone, methyl isobutyl ketone) could not be used because they caused the tubing of the peristaltic pump to swell. Aromatic solvents (toluene, xylene) were found to lead to highly luminous flames outside the plasma region and to generate a rather high background signal. Ultimately, the choice fell to a high-bp petroleum ether (boiling range 200-250 C).

This solvent, commercially referred to as kerosene, also burns outside the plasma region but rather modestly. It also shows a background signal that is much higher than water. Both factors, the dilution and solvent background signal, cause the analysis of trace elements in oil to be less sensitive than the analysis of trace elements in water by a factor of about 5.

Dilution Factor

As already indicated, diluting the oil with kerosene ensures a stable nebulization but reduces the signal intensity. Obviously, an optimal dilution factor must exist but it is also evident that this optimum depends on the element to be analyzed and its concentration. In general, low concentrations and elements that have a low signal-to-background ratio require little dilution.

For practical purposes and routine analyses, a standard dilution factor is preferred which permits analyses of low concentrations. Nonroutine analyses may employ different factors that result from specific optimizations.

A standard dilution factor has been chosen on the basis of a number of experiments in which the element to be determined, its concentration and the dilution factor were the independent variables and in which the measurement result, its standard deviation, the spread of the individual measurements and the number of counts/concentration were determined. Table II gives an example of such a series of measurements that were done using copper as the element. The high standard used to calibrate the instrument contained 400 ppb of copper whereas the low standard contained 10 ppb. The samples were analyzed at a wavelength of 324.7 nm using input and output slits of 25/300 (see explanation in next section). Concentrations are expressed on the oil before dilution and thus are not affected by diluting the oil. The dilution factor has been expressed on a w/v basis for accuracy and convenience. Weighing the oil is the most accurate way of defining a quantity of oil and measuring kerosene can be done both accurately and fast using a pipette.

As expected, the number of counts/100 ppb decreases with increased dilution because the background signal increases. At a dilution factor of 1:4 (w/v), the standard deviation of the measurements has increased over values observed at lower dilutions. Similar experiments with other elements also demonstrate that a 1:4 dilution decreases reproducibility so that for subsequent routine analyses, a dilution factor of 1:2 was chosen. For practical purposes, this dilution also has the advantage that partially hydrogenated oils need not be heated to their melting points but dissolve at a lower temperature. This is especially important if residual nickel has to be determined when studying catalyst filtration efficiency.

Slits

The background signal is continuous whereas the light emitted by elements is at precise wavelengths. Narrowing the slit will therefore increase the element-to-background signal ratio and thus increase sensitivity. On the other hand, using a narrow slit requires accurate positioning of plasma, echelle grating and prism, and makes the instrument more sensitive to thermal drift.

To determine the effect of slit size, measurements were made at several slits provided on the instrument. Slits are characterized by 2 figures separated by a stroke indicating slit width and slit height, respectively, expressed in μ. The data given in Table III again refer to copper measured at 324.7 nm using a dilution factor of 1:2. In all experiments, input and output slit dimensions were the same.

A smaller slit causes the standard deviation and the spread to decrease and the number of counts/100 ppb copper in the oil to increase as illustrated by Table III. At a slit size of 200/300, the number of counts/100 ppb is about 260; this figure increases to 460 at a slit size of 50/300. A further increase would be expected at a slit size

TABLE II

Measurements of Copper in Oil at Several Dilutions

Dilution factor (w/v)	Concentration Actual (ppb)	Concentration Measured (ppb)	St. dev. (ppb)	Spread (counts)	Counts/ 400 ppb
1:1	201	219	4	37	591
1:1	101	111	4	39	573
1:1	50	55.2	6	62	600
1:1	25	21.0	5	56	590
1:1	10	9.9	5	43	595
1:2	201	201	2	14	450
1:2	101	98.2	7	56	452
1:2	50	40.4	6	52	452
1:2	25	19.7	2	15	461
1:2	10	7.6	6	51	459
1:4	201	217	15	83	325
1:4	101	120	14	89	346
1:4	50	56	10	56	338
1:4	25	32	5	26	347
1:4	10	-0.6	10	91	343

TABLE III

Measurements of Copper in Oil at Various Slit Dimensions

Slit	Concentration Actual (ppb)	 Measured (ppb)	 St. dev. (ppb)	Spread (counts)	Counts/ 100 ppb
200/300	201	197	21	98	255
200/300	101	117	9	40	257
200/300	50	60	16	83	278
200/300	25	9.3	9	43	267
100/300	201	190	9	52	330
100/300	101	101	11	70	332
100/300	50	58.5	8	48	338
100/300	25	5.6	10	61	326
50/300	201	192	10	85	463
50/300	101	91	3	25	475
50/300	50	51.7	5	43	441
50/300	25	21.7	2	17	459
50/300	10	4.1	7	85	460
25/300	201	193	5	35	418
25/300	101	96.2	14	109	421
25/300	50	34.7	1	6	422
25/300	25	17.4	4	30	416
25/300	10	5.5	3	24	422
50/500	201	184	4	30	436
50/500	101	84	11	80	430
50/500	50	48	6	44	424
50/500	25	15	9	70	424
50/500	10	14.5	7	56	432
10/500	201	183	7	55	467
10/500	101	101	10	86	449
10/500	50	47	2	16	471
10/500	25	21	3	19	457
10/500	10	10.7	8	68	471

of 25/300, but has not been observed during this series of measurements. A partial explanation of this phenomenon lies in the fact that the amplifier gain chosen for the smallest slit size was such that the number of counts corresponding to the high standard happened to be lower than when the wider slits were used. Another reason could well be that the positioning of plasma, echelle grating and prism has become very sensitive so that slight maladjustments cause the number of counts to be reduced sharply.

Therefore, a slit size of 50/300 is used for routine measurements, this size being a compromise between sensitivity and ease of operation. Measurements close to the detection limit or requiring high accuracy tend to use smaller slit sizes.

Linearity

Because results are obtained by linear interpolation between high and low standards, a linearity of the measurement is assumed and has to be checked. This was done by preparing a number of samples with known amounts of phosphorus and by comparing actual and measured values. The high standard in this experiment contained 500 ppm P. Measurements were done at 213.6 nm with two 100/300 slits; the duration of a single measurement was 10 sec and they were repeated 3 times.

The results in Table IV show the differences between actual and measured values to be small and, because their signs are random, the linearity can be concluded to be good.

The standard deviations given in Table IV are rather high because of the high concentration of the high standard. If low concentrations must be measured more reproducibly, it is advantageous to use a high standard with a lower concentration and a narrower slit. Table V illustrates what can be achieved if a high standard with 5 ppm phosphorus and a 25/300 slit is used.

Wavelength and Detection Limits

The instrument manufacturer has provided a list of "best strongest lines and interferences" and of "linear weaker lines and interferences." These lists have been used as an initial guide in choosing the wavelengths most appropriate for the measurements of trace elements in edible oil, but

TABLE IV

Linearity of Measurement
(High Standard 500 ppm Phosphorus)

Actual (ppm)	Measured (ppm)	St. dev. (ppm)	Difference Abs. (ppm)	 Rel. (%)
200	205	2.2	+ 5	+ 2.5
100	100	1.0	–	0
75	76.2	0.6	+ 1.2	+ 1.6
50	49.9	0.6	- 0.1	- 0.2
25	26.3	1.9	+ 1.3	+ 5.2
10	10.5	0.9	+ 0.5	+ 5.0
5	6.2	0.5	+ 1.2	+ 24.0
2.5	1.6	0.3	- 0.9	- 36.0

TABLE V

Linearity of Measurement
(High Standard 5 ppm Phosphorus

Actual (ppm)	Measured (ppm)	St. dev. (ppm)	Differences Abs. (ppm)	 Rel. (%)
4	3.8	0.2	0.2	5.0
2	1.8	0.2	0.2	10
1	1.1	0.2	0.1	10
0.5	0.4	0.1	0.1	20

TABLE VI

Response as Function of Wavelength for Phosphorus

Wavelength (nm)	Dilution factor (w:v)	Slit	No. of counts/ ppm P
213.6	1:1	200/300	110
213.6	1:1	50/300	190
213.6	1:2	200/300	90
213.6	1:2	50/300	170
213.6	1:4	200/300	50
213.6	1:4	50/300	140
214.9	1:1	200/300	65
214.9	1:1	50/300	100
214.9	1:2	200/300	55
214.9	1:2	50/300	100
253.4	1:2	50/300	2
255.3	1:2	50/300	10

wavelengths reported in the literature have been tried, as well. In choosing the preferred wavelength, the number of counts/unit of concentration has been used as selection criterion. For phosphorus, 4 wavelengths have been studied at several dilution factors and slit sizes. The results are given in Table VI. On the basis of these results, the wavelength chosen for the element phosphorus is 213.6 nm. For other elements, similar studies have been done for which the results have been listed in Table VII. In Table VII, the detection limits have also been listed, whereby this limit has been calculated as twice the standard deviation as observed when measuring low concentrations.

TABLE VII

Optimal Wavlengths

Element	Wavelength (nm)	Detection limits
P	213.6	0.5 ppm
Cu	324.7	5 ppb
Ni	231.6	70 ppb
Fe	259.9	50 ppb
Si	288.1	50 ppb
Hg	253.6	150 ppb
Pb	283.3	100 ppb

Running Costs

The plasma emission spectrometer used in this study uses welding grade argon at the rate of about 14 L/min, which is the most expensive element in the running costs. The electrodes last about 2-4 days if the equipment is used almost continuously.

Stability

When the instrument is set up for a series of measurements and high and low standards have been input, and if the high standard is then offered at regular intervals to the instrument as a sample to be measured, the same values should result from each measurement. In practice, this is not always the case. Values may remain constant for some time and then drift away to a different value. Naturally, attempts have been made to find the cause of this lack of stability and although some potential causes have emerged, the lack of long-term stability has not been remedied. One cause lies in the improved nebulization efficiency when the nebulizer is warmed by radiant heat from the plasma. It has therefore become standard practice to light the plasma 15 min prior to the start of the measurements.

Another cause, leading to a sudden drop in measured values, has been detected in a partial blockage of the aspirator tube of the nebulizer. Hardened oils and oils with suspending matter are naturally more prone to cause such blockages than perfectly clear liquid oils.

Although other potential causes such as changes in ambient temperature and fluctuations in the voltage of the power supply have been investigated, it has as yet not been possible to guarantee long-term stability of the measurement. Consequently, a measurement procedure has been adopted that eliminates rogue results. This procedure entails the measurement of both high and low standard after 10-15 samples have been measured. If the values found for both standards deviate significantly from their true values, the measurements on the samples are repeated. If the deviation is quite large, the aspirator tube of the nebulizer is checked for cleanliness. In practice, the lack of long-term stability, which has not only been observed with edible oils but also with aqueous solutions, is not a serious drawback; repeat of measurements is not often necessary. The procedure as described is, however, essential to guard against spurious results that might otherwise go undetected.

DISCUSSION

Plasma emission spectrometry has been found to be a fast, accurate and sensitive analytical method of determining trace elements in edible oils. Detection limits are not as low as reported for aqueous solutions because it is necessary to dilute the oil with a solvent which not only lowers the concentration of the element but also generates a background signal.

In comparison to existing methods, analysis by plasma emission spectroscopy is considered to be a valuable improvement. Measurements that were hitherto labor-intensive and only carried out if absolutely necessary can now become readily available and thus facilitate a deeper insight into oil refining processes and oil quality. Sensitivity, linearity and reproducibility are far superior to what is needed in practice, provided a procedure is adopted that detects a drift in output signal and prescribes corrective measures.

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Letter to the Editor

Sir:

The term "selectivity" (SR), when used in reference to a hydrogenated oil or a hydrogenation catalyst, has come to mean the ratio of 2 reaction rates, the rate of hydrogenation of linoleic acid, a diene, divided by the rate of hydrogenation of oleic acid, monoene. The SR may be used as a criterion for catalyst selection and also processing conditions.

To determine the SR, hydrogenation of an oil using a specific set of processing conditions and catalyst is accomplished. The fatty acid composition of the starting and ending samples is determined and from those data and a computer, the reaction rates may be calculated and the SR determined. Because a computer is not always available, Albright (1) published a set of curves he had calculated so that the SR could be found from these graphs. However, the hydrogenation must be continued for some time to enable one to use the graphs. Also, the linolenic selectivity (LnSR) curves published by Allen (2) require a calculation before the graphs can be used.

Unfortunately, the reaction rate equations used to calculate the selectivities do not have closed solutions, so the calculation is accomplished by an iterative process which needs considerable speed and memory in a computer; the small computers and calculators now available are too slow.

Thus, there is a need for a rapid, simple method to calculate SR and LnSR from fatty acid composition data using a calculator.

The graphs published by Albright for the estimation of Selectivity Ratio by the hydrogenation of soybean oil are a family of lines. Such a family may be expressed as shown in Equation I, where S_O, S are the starting and ending stearic content, and L_O, L, the starting and ending linoleic. Albright's data for the SR of soybean oil were used to substitute into the equation and the 4 constants were calculated. Thus, for soybean oil the equation becomes:

$$SR = (100\ S\text{-}S_O)[1/((1.2603(Exp(2.0652(L/L_O))))\text{-}(.07713)(Exp(\text{-}2.2988(L/L_O))))]$$

This expression may be evaluated by a good calculator.

Also, the functional form of the Linolenic Selectivity (LnSR) curves calculated by Allen may be expressed as:

$$L/L_O = (Ln/Ln_O)^b,$$

$$SR = \frac{100}{S - S_o}\left[\frac{1.0}{ae^{b\left(\frac{L}{L_o}\right)} - ce^{-d\left(\frac{L}{L_o}\right)}}\right]$$

$$a = 1.260 \qquad c = 0.771$$

$$b = 2.065 \qquad d = 2.299$$

Equation I

where b is a function of the LnSR. The LnSR constants are inversely proportional to the estimated (b) and 2 coefficients are necessary to obtain the LnSR constants. The constants were evaluated by linear regression from knowns for soybean oil hydrogenation. Thus, the equation becomes:

$$LnSR = (0.6989\ (1n\ \frac{Ln}{Ln_O}/1n\ \frac{L}{L_O})) + .3011,$$

where Ln_O, Ln are start and ending linolenic and L_O, L are the linoleic acid in soybean oil.

These equations permit the calculation of the SR and LnSR by a calculator from the fatty acid composition of the starting and ending hydrogenated samples of soybean oil.

Table I shows the results of calculation of the SR and LnSR by a computer evaluation of reaction rate constants and the results obtained from the equations solved by a TI-59 calculator. As shown, the results are comparable. The program for the TI-59 calculator is available from the author.

R.R. ALLEN
Rt. 7, Box 44
McKinney, TX 75069

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TABLE I

Fatty acid composition						SR		Ln SR	
S_O	S	L_O	L	Ln_O	Ln	Computer	Calculator	Computer	Calculator
4.44	4.67	51.12	32.61	6.74	1.99	94.6	96.0	2.2	2.2
4.44	4.79	51.12	34.46	6.74	0.09	58.0	58.2	8.1	8.0
4.44	9.57	51.12	42.30	6.74	0.01	3.2	3.6	14.2	14.1
4.44	7.00	51.12	45.20	6.74	0.05	7.1	7.3	10.4	10.6
4.44	6.74	51.12	37.40	6.74	0.10	31.1	32.1	9.4	9.7