

Analysis of air

Some of the common polluting agents can be analysed by Voltammetry: some heavy metals and some reducing or oxidising compound can be analysed by using mercury or graphite or gold electrodes.

Metals are determined by dissolving the powder collected on a cellulose filter, while organic substances are adsorbed by bubbling the air into specific solutions.

Apparatus, reagents and procedures are stated in specific national (or EC) laws and regulations.

Analysis of lead and heavy metals

Principle of the method

According to the EC rules about the analysis of lead in the air powder, the metal suspended in the air is collected on a micropores membrane by filtering a known volume of air. After an acidic digestion with nitric acid, lead is analysed in the solution.

Interference

Tin at similar concentration of lead.

Reagents

- 65% Nitric acid for trace heavy metals analysis (lead content less than 70 ug/l)
- Distilled water for trace heavy metals analysis
- Supporting electrolyte: 0.1 M $\text{H}_2\text{C}_2\text{O}_4$ and 0.2 M HCl solution

Dissolve 9 g of $\text{H}_2\text{C}_2\text{O}_4$ (or 12.6 g of $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$) and 16.7 ml of 37% HCl in 1 l of distilled water. Store in a polythene bottle.

- Lead concentrated standard solution (0.1 g/l)

Dissolve 0.1599 g of $\text{Pb}(\text{NO}_3)_2$ (pure and dried), in 1 l of 1 % HCl, in a volumetric flask. (MM $\text{Pb}(\text{NO}_3)_2 = 331.21$; MMPb = 207.2).

- Lead working standard solution (1 mg/l)

Dilute 1 ml of 0.1 g/l Pb standard solution in 100 ml of distilled water, in a volumetric flask.

Apparatus

- 50 mm diameter membrane filter with micropores from 0,4 and 0,5 micron. Filter must exhibit a collecting efficiency upper to 99% for every particles having a mean aerodynamic diameter of 0.3 μm , at the speed of the sampling device. Filter must not deteriorate itself during the sampling time and must be completely dissolved after the following procedure.

Do not use PTFE filter because the residue after boiling with 37% HCL can not be easily mineralised.

- Sampling device:
 - Filtration set, according to the specific national regulations
 - Aspirating pump having a flow load of 20 l/min, accordingly to the specific national regulations
 - Volumetric measurer, according to the specific national regulations

Efficiency of the sample device is determined by the ratio of the mass concentration of the particles collected on the filter and the concentration of the particles in the atmosphere.

Efficiency must be greater than the values reported in the following table and must be independent from the wind direction.

***Minimum admissible efficiency (%)
for a sample device***

Wind force	Particle dimension (aerodynamic diameter)	
	5 μm	10 μm
2 $\text{m}\cdot\text{s}^{-1}$	95 %	65 %
4 $\text{m}\cdot\text{s}^{-1}$	95 %	60 %
6 $\text{m}\cdot\text{s}^{-1}$	85 %	40 %

- Labware lead free, accurately washed with 1+1 HCl.
- Hotplate

Sampling procedure

Every components of the sampling line must be set like stated in specific national regulation. Usually the following order is appointed:

- filter support
- aspirating pump and flow rate regulator
- volumetric counter

Filter is placed on the support and the sampling is start with a 20 l/min flow rate. The filter support must be oriented downwards.

Aspirating flow rate must be maintained constant during all the sampling time with a tolerance of 5% of the nominal value.

The speed of the air on the surface of the filter has to be between 33 and 55 cm/s.

At the end of the sampling, the filter must be put in a specific, closed container.

Stop the sampling procedure after 24 hours.

Filter digestion on a hotplate

Fold the filter and place it into the polarographic cell.

Add 3 ml of 65% HNO_3 and 2 ml of 40% H_2O_2 . Let stand overnight.

Bring to dryness on a sand bath or an hotplate, avoiding to exceed 200°C.

Add 1 ml of 65% HNO_3 and 2 ml of 40% H_2O_2 and bring to dryness again.

Repeat the treatment until residue is white (not black, nor brown, nor yellow!)

Add 10 ml of supporting electrolyte.

Alternatively, use a microwave digester but bring to dryness the residue.

Blank analysis

Digest a clean filter as described above.

Voltammetric analysis

Follow the indication described in the lead data sheet.

Calculation of the concentration of lead in the air

Use the following relation:

$$C_{Pb} = \frac{(C_s - C_b) \cdot 10^{-2}}{V}$$

dove:

C_{Pb} lead concentration in air, ($\mu\text{g}/\text{m}^3$);

C_s lead concentration in the sample solution, ($\mu\text{g}/\text{L}$);

C_b lead concentration in the blank solution, ($\mu\text{g}/\text{L}$);

V volume of sampled air, at 25 °C and at 1013 millibar, (m^3).

This procedure can be used for the analysis of Cadmium and Copper, in the same solution.

Finally, this procedure can be used for the analysis of the following metals, changing the supporting electrolyte (see every specific data sheet):

<i>Element</i>	<i>Supporting electrolyte</i>
Ni e Co	0.1 M tartrate buffer, pH 9 + Dimetilglioxime
Pd	0.1 M acetate buffer, pH 5.15 + Dimetilglioxime
Pt	H ₂ SO ₄ + formaldehyde + hydrazine
Zn	0.1 M acetate buffer, pH 4.5

Lead in the air of a street in Milan

Concentration in the sample solution = 1.9 $\mu\text{g/l}$

Concentration in the air = 38 ng/m^3

Method: 5 additions

Volumes Table

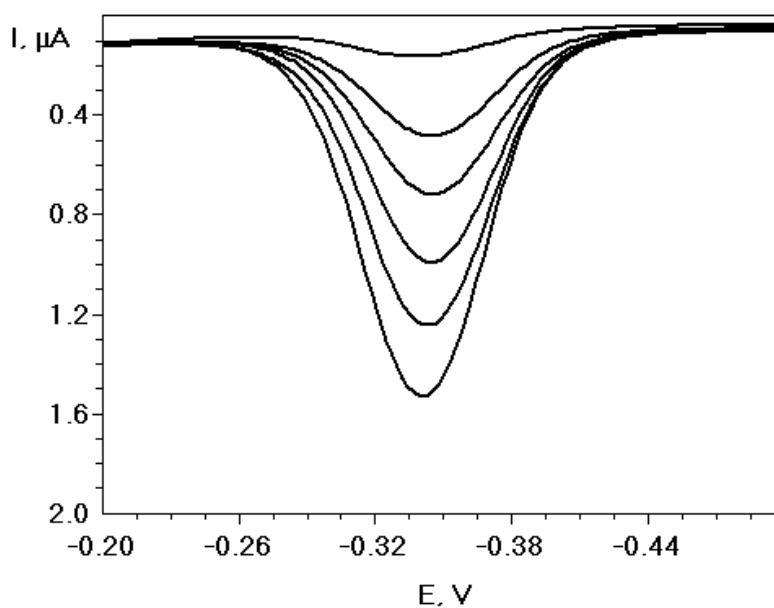
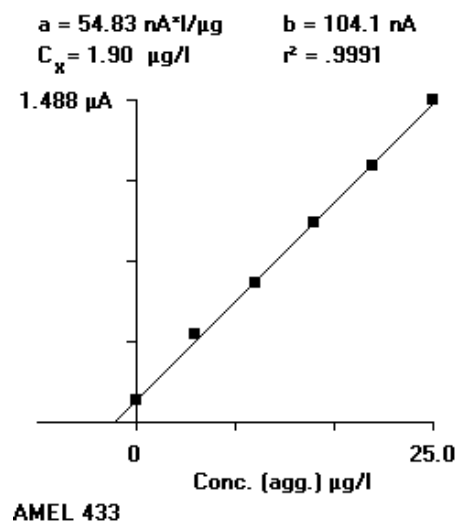
Solvent Volume	0 (ml)
Supporting Sol.	0 (ml)
Sample Weight	10 (g)
Standard Conc.	1000 ($\mu\text{g/l}$)

Height Table

#	Peak Pot.	Height
0	-342.1	97.45 nA
1	-344.4	398.9 nA
2	-345.8	632.8 nA
3	-344.4	911.1 nA
4	-342.1	1.162 μA
5	-341.1	1.452 μA

Regression Data

#	Add. Conc.	Height x dilution	
0	0 $\mu\text{g/l}$	97.45 nA	$y = ax + b$
1	5.00 "	400.9 nA	$a = 54.83 \text{ nA} \cdot \text{l} / \mu\text{g}$
2	10.0 "	639.2 nA	$b = 104.1 \text{ nA}$
3	15.0 "	924.9 nA	$r^2 = .9991$
4	20.0 "	1.186 μA	
5	25.0 "	1.488 μA	



Lead in the air of a paint plant

Concentration in the sample solution = 573 $\mu\text{g/l}$

Concentration in the air: 8.2 $\mu\text{g/m}^3$

Method: 5 additions

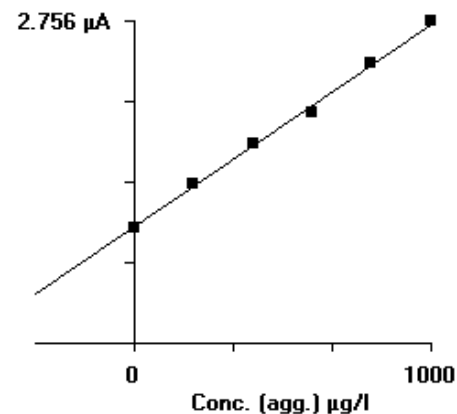
Volumes Table

Solvent Volume	0 (ml)
Supporting Sol.	0 (ml)
Sample Weight	10 (g)
Standard Conc.	10000 ($\mu\text{g/l}$)

Height Table

#	Peak Pot.	Height
0	-334.5	989.3 nA
1	-335.8	1.341 μA
2	-332.1	1.649 μA
3	-332.1	1.864 μA
4	-331.2	2.217 μA
5	-329.8	2.505 μA

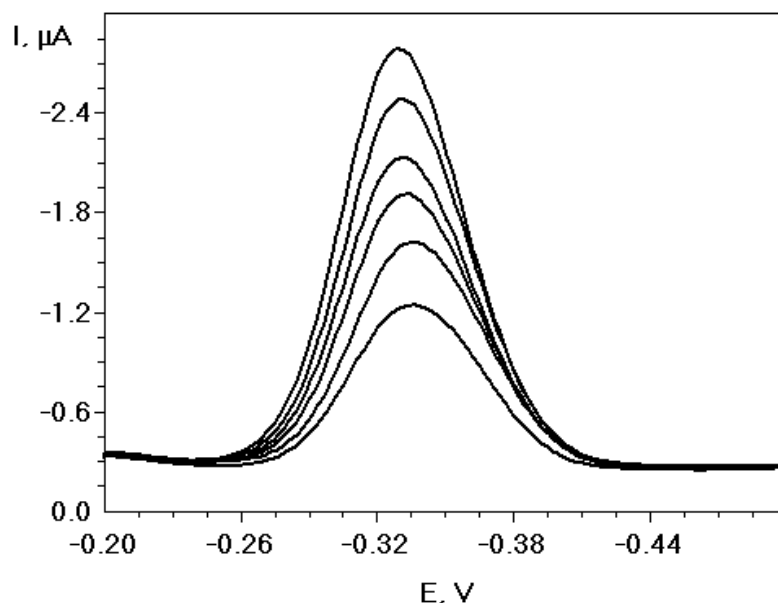
$a = 1.739 \text{ nA}^*/\mu\text{g}$ $b = 997.0 \text{ nA}$
 $C_x = 573 \mu\text{g/l}$ $r^2 = .9973$



AMEL 433

Regression Data

#	Add. Conc.	Height x dilution	
0	0 $\mu\text{g/l}$	989.3 nA	$y = ax + b$
1	200 "	1.368 μA	$a = 1.739 \text{ nA}^*/\mu\text{g}$
2	400 "	1.715 μA	$b = 997.0 \text{ nA}$
3	600 "	1.976 μA	$r^2 = .9973$
4	800 "	2.395 μA	
5	1000 "	2.756 μA	



Palladium

Method: 0.1 M Dimethylglyoxime in acetate buffer, pH 5.15

Function: Differential Pulse Stripping Voltammetry (DPS/a)

Start Potential (mV)	-200
End Potential (mV)	-1000
Current range	1,024 μ A
Scan Speed (mV/s)	50
Deposition time (s)	120
Deposition Pot. (mV)	-200
Number of cycles	2
Delay before sweep (s)	5
Purge and stir time (s)	300
Stirring speed (rpm)	300
Drop Size (a.u.)	60

Palladium concentrated standard Solution (1 g/l)

Dissolve 0.1 g of pure Pd in 5 ml of aqua regia (37% HCl + 65% HNO₃, 3+1, v/v). Bring to dryness. Add of 37% HCl and 25 ml of distilled water. Heat gently, until salts are completely dissolved. Dilute to 100 ml with distilled water, in a volumetric flask.

Supporting electrolyte

1- 1 M acetate buffer, pH 5.15

Dissolve 13.6 g of CH₃COONa · 3H₂O (or 8.2 g of anhydrous CH₃COONa) in 50 ml of distilled water, add 20% NaOH till pH 5.15. Dilute to 100 ml with distilled water, in a volumetric flask.

2- 0.1 % Dimethylglyoxime in ethanol (p/v)

Dissolve 0.1 g of Dimethylglyoxime in 100 ml of ethanol. Prepare a fresh solution at the moment of the analysis.

Procedure

Add to 10 ml of sample, 1 ml of buffer and 0.1 ml of dimethylglyoxime solution. Check that pH is 5.15. If necessary, correct by using NaOH or CH₃COOH.

Diluted standard solution (1 mg/l)

Dilute 1 + 999 the concentrated standard solution of Pd in distilled water. Prepare the solution at the moment of the analysis

Working standard solution (100 μ g/l)

In a 50 ml volumetric flask, add 5 ml of buffer, 0.5 ml of dimethylglyoxime solution and 5 ml of diluted standard solution. Bring to volume with distilled water. Wait for 30 min before the use. Prepare the solution at the moment of the analysis.

Palladium in the air of a street in Milan

Sample Concentration = 0.64 mg Pd/kg of powder
 = 92 ng Pd on the filter
 = 0.32 $\mu\text{g}/\text{m}^3$ in the air

Method: 4 additions

Volumes Table

Solvent Volume	0 (ml)
Supporting Sol.	11.1 (ml)
Sample Weight	0.143 (g)
Standard Conc.	0.1 (mg/l)

Height Table

#	Peak Pot.	Height
0	-593	145.0 nA
1	-610.7	428.5 nA
2	-606.8	622.0 nA
3	-616.2	749.4 nA
4	-616.2	881.9 nA

Regression Data

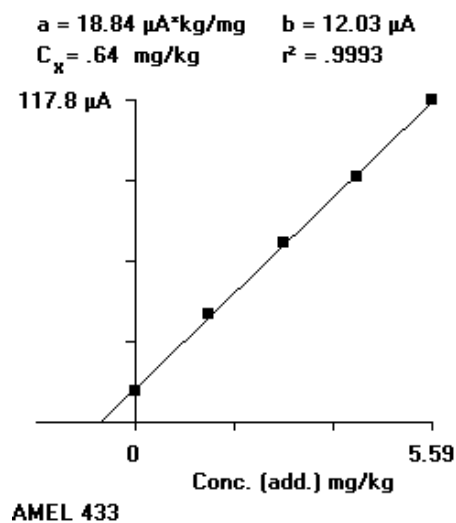
#	Add. Conc.	Height x dilution
0	0 mg/kg	11.26 μA
1	1.40 "	39.26 μA
2	2.80 "	65.68 μA
3	4.20 "	89.62 μA
4	5.59 "	117.8 μA

$$y = ax + b$$

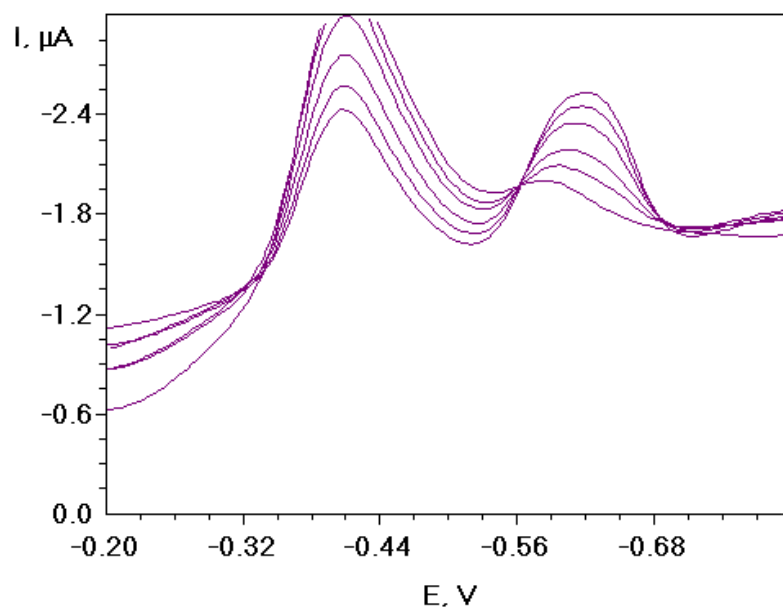
$$a = 18.84 \mu\text{A} \cdot \text{kg}/\text{mg}$$

$$b = 12.03 \mu\text{A}$$

$$r^2 = .9993$$



AMEL 433



Platinum in the air of a street of Milan

Sample Concentration = 367 ng/l in the solution
 = 12.7 ng/m³ in the air

Method: 3 addition

Volumes Table

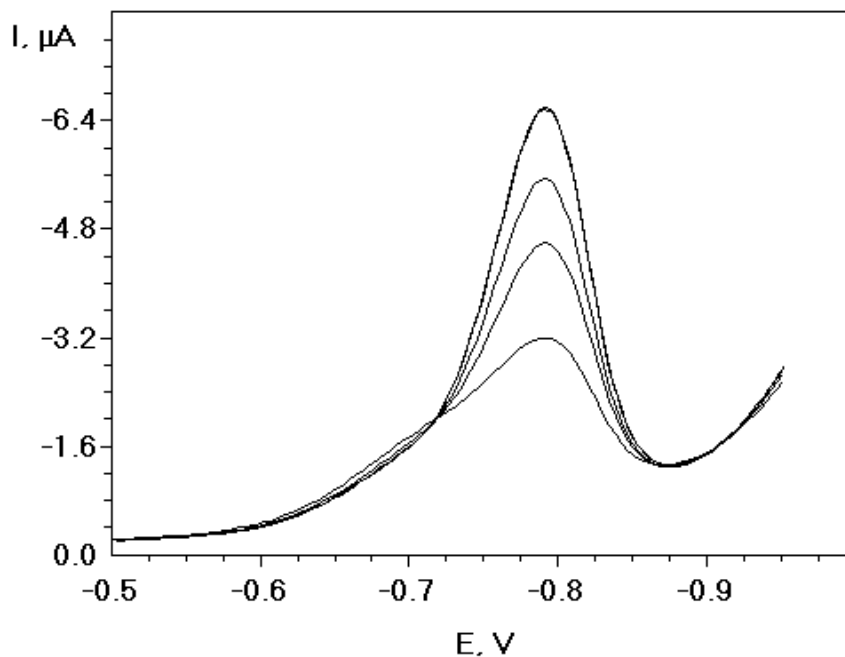
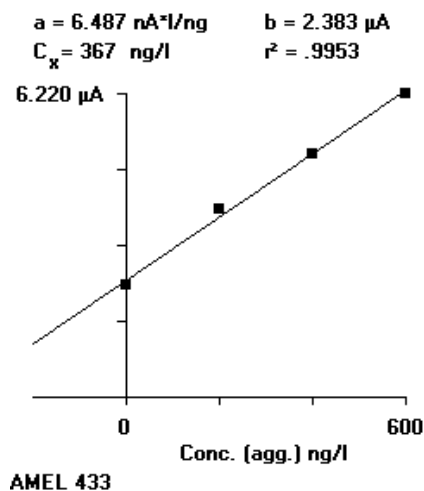
Solvent Volume	0 (ml)
Supporting Sol.	0.52 (ml)
Sample Volume	10 (ml)
Standard Conc.	10000 (ng/l)

Height Table

#	Peak Pot.	Height
0	-788.2	2.163 μA
1	-792.1	3.581 μA
2	-788.2	4.560 μA
3	-792.1	5.593 μA

Regression Data

#	Add. Conc.	Height x dilution	
0	0 ng/l	2.276 μA	$y = ax + b$
1	200 "	3.839 μA	$a = 6.487 \text{ nA}^*1/\text{ng}$
2	400 "	4.980 μA	$b = 2.383 \mu\text{A}$
3	600 "	6.220 μA	$r^2 = .9953$



Formaldehyde

Method: Hydrazine in 0.1 M citrate buffer, pH 6.5

Technique: Differential Pulse Voltammetry (DPV/a)

Start Potential	(mV)	-600
End Potential	(mV)	-1300
Current range		2.048 μ A
Scan Speed	(mV/s)	3
Number of cycles		5
Delay before sweep	(s)	10
Purge and stir time	(s)	300
Stirring speed	(rpm)	60
Drop Size	(a.u.)	60

Formaldehyde concentrated standard solution (1 g/l)

Dilute 2.74 ml of 36.5 % Formaldehyde in 1 l of distilled water in a volumetric flask.

Prepare fresh solution at the moment of analysis. Titrate the solution as described in the next page.

Supporting Electrolyte

1- 1 M ammonium citrate buffer at pH 6.5. Dissolve 21 g of mono hydrate citric acid in 80 of distilled water. Adjust pH to 6.5 by using conc. NH_3 . Bring to the mark in a 100 ml volumetric flask with distilled water.

2- 1% Hydrazine sulphate aqueous solution. Prepare fresh solution at the moment of analysis

Procedure

Pour 10 ml of sample in the cell, add 1 ml of ammonium citrate buffer. Deaerate for 10 min. Add 1 ml of hydrazine solution.

Working standard solution (10 mg/l)

Dilute the concentrated standard solution 1+99 in, at the moment of the analysis.

Interference

High concentration of other aldehydes can overlap the peak of the formaldehyde.

Zinc can overlap the formaldehyde peak: use clean reagents.

Alternative supporting electrolytes

0.1 M ammonium phosphate buffer, pH 6.5 – pay attention to the presence of zinc in this reagent !

0.36 M sulphuric acid – lower sensitivity and worse base line can be performed with this reagent.

Analysis of formaldehyde in the air

Sample the air in a bubbler filled with in 25 ml of 0.1 M citrate buffer solution for 1 – 2 hour using a pump, with a flow of 1 ml/ min.

Pour the solution in a 25 ml volumetric flask and bring to volume with a 0.1 M citrate buffer solution.

Use 10 ml of his solution for the voltammetric analysis.

Titration of the concentrated standard solution of formaldehyde

Pour 5 ml of fresh 1.13 M Na_2SO_3 solution (142.3 g/l), in a 50 ml beaker.

Adjust pH between 8.5 and 10 with NaOH or HCl.

Record the final pH.

Add 10 ml of concentrated standard solution of formaldehyde. The pH should be greater than 11.

Titrate the solution back to the pH recorded before with 0.02 N H_2SO_4 (about 17 ml are needed).

If pH is overrun, back titrate again with 0.01 M NaOH.

Calculate the concentration of the solution:

$$C \text{ (mg / ml)} = \frac{30 \cdot (N_{\text{H}_2\text{SO}_4} \cdot V_{\text{H}_2\text{SO}_4} - N_{\text{NaOH}} \cdot V_{\text{NaOH}})}{V_{\text{conc. std. sol.}}}$$
$$= 3 \cdot (N_{\text{H}_2\text{SO}_4} \cdot V_{\text{H}_2\text{SO}_4} - N_{\text{NaOH}} \cdot V_{\text{NaOH}})$$

Analytical report

Analysis: Air of the lab

Sample (solution) Concentration = 71 $\mu\text{g/l}$

Sample (air) Concentration = 33 $\mu\text{g/m}^3$

Method: 5 addition and blank subtraction

Volumes Table

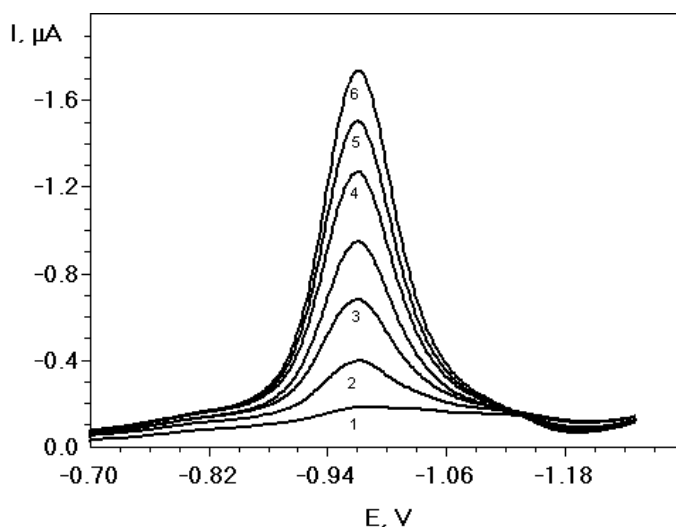
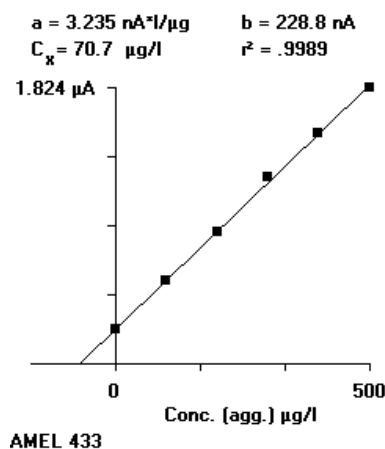
Solvent Volume	0 (ml)
Supporting Sol.	1 (ml)
Sample Volume	10 (ml)
Standard Conc.	10000 ($\mu\text{g/l}$)

Height Table

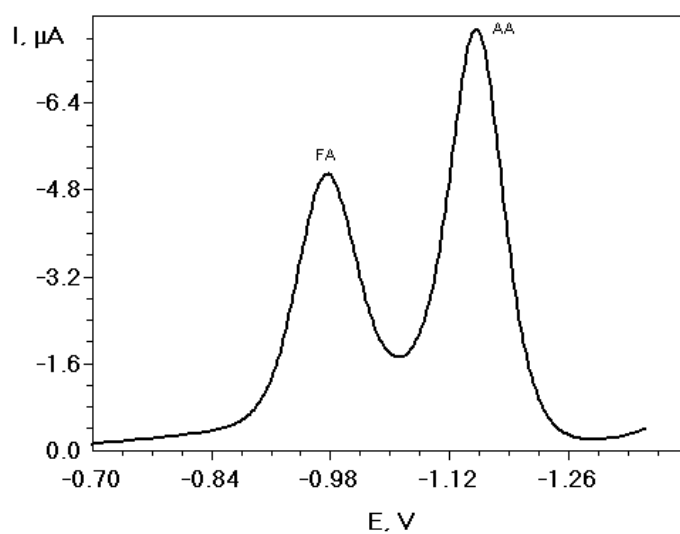
#	Peak Pot.	Height
0	-968.6	204.1 nA
1	-968.6	489.5 nA
2	-970	776.3 nA
3	-968.6	1.091 μA
4	-968.6	1.342 μA
5	-970.9	1.586 μA

Regression Data

#	Add. Conc.	Height x dilution	
0	0 $\mu\text{g/l}$	224.5 nA	$y = ax + b$
1	100 "	543.4 nA	$a = 3.235 \text{ nA}^*/\mu\text{g}$
2	200 "	869.5 nA	$b = 228.8 \text{ nA}$
3	300 "	1.234 μA	$r^2 = .9989$
4	400 "	1.530 μA	
5	500 "	1.824 μA	



1= Blank; 2= Sample; 3, 4, 5, 6, 7 = standard sol. additions



The procedure can be used also for the analysis of the other total aldehydes, even if formaldehyde has to be present at low concentration.

FA = formaldehyde; AA= Acetaldehyde (total aldehydes)

Total aldehydes

Method: Hydrazine in 0.1 M citrate buffer, pH 6.5

Technique: Differential Pulse Voltammetry (DPV/a)

Start Potential	(mV)	-1000
End Potential	(mV)	-1350
Current range		2.048 μ A
Scan Speed	(mV/s)	3
Number of cycles		5
Delay before sweep	(s)	10
Purge and stir time	(s)	300
Stirring speed	(rpm)	60
Drop Size	(a.u.)	60

Use this procedure for the analysis of formaldehydes and total aldehydes. The first shows a peak potential at about -970 mV, while the latter appear like a unique peak at about -1150 mV. Total aldehydes are analysed by using acetaldehyde as reference standard.

Total aldehydes concentrated standard solution (1 g/l)

Dissolve 1 g of pure acetaldehyde in 1 l of distilled water in a volumetric flask.

Prepare fresh solution at the moment of analysis.

Supporting Electrolyte

1- 1 M ammonium citrate buffer at pH 6.5. Dissolve 21 g of mono hydrate citric acid in 80 of distilled water. Adjust pH to 6.5 by using conc. NH_3 . Bring to the mark in a 100 ml volumetric flask with distilled water.

2- 1% Hydrazine sulphate aqueous solution. Prepare fresh solution at the moment of analysis

Procedure

Pour 10 ml of sample in the cell, add 1 ml of ammonium citrate buffer. Deaerate for 10 min. Add 1 ml of hydrazine solution.

Working standard solution (10 mg/l)

Dilute the concentrated standard solution 1+99 in, at the moment of the analysis.

Interference

High concentration of formaldehydes can mask the peak of the total aldehydes.

Alternative supporting electrolytes

0.1 M ammonium phosphate buffer, pH 6.5

Analysis of total aldehydes in the air

Sample the air in a bubbler filled with in 25 ml of 0.1 M citrate buffer solution for 1 – 2 hour using a pump, with a flow of 1 ml/ min.

Pour the solution in a 25 ml volumetric flask and bring to volume with 0.1 M citrate buffer solution.

Use 10 ml of his solution for the voltammetric analysis.

Analytical report

Analysis: Air of the lab

Sample (solution) Concentration = 27 $\mu\text{g/l}$

Sample (air) Concentration = 8 $\mu\text{g/m}^3$

Method: 5 addition and blank subtraction

Volumes Table

Solvent Volume	0 (ml)
Supporting Sol.	1 (ml)
Sample Volume	10 (ml)
Standard Conc.	10000 ($\mu\text{g/l}$)

Height Table

#	Peak Pot.	Height
0	-1115.6	30.36 nA
1	-1113.3	61.55 nA
2	-1115.6	95.35 nA
3	-1116.5	126.7 nA
4	-1114.2	161.6 nA
5	-1115.6	192.7 nA

Regression Data

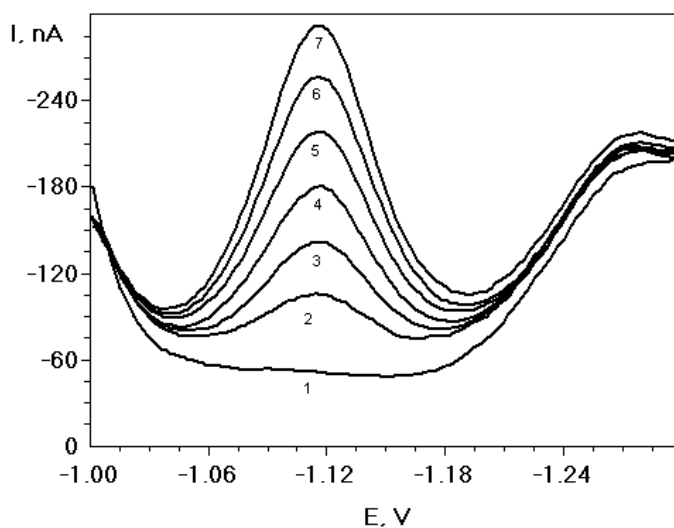
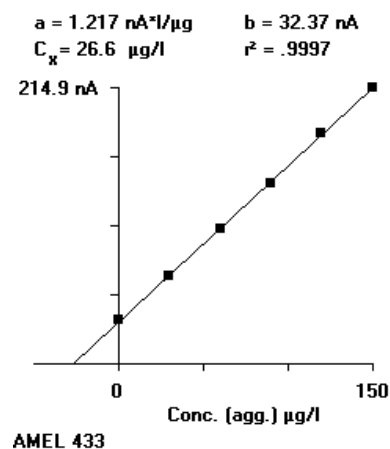
#	Add. Conc.	Height x dilution
0	0 $\mu\text{g/l}$	33.40 nA
1	30.0 "	67.90 nA
2	60.0 "	105.5 nA
3	90.0 "	140.5 nA
4	120 "	179.7 nA
5	150 "	214.9 nA

$$y = ax + b$$

$$a = 1.217 \text{ nA}^*/\mu\text{g}$$

$$b = 32.37 \text{ nA}$$

$$r^2 = .9997$$



1= Blank; 2= Sample; 3, 4, 5, 6, 7 = standard sol. additions