OPTIMIZATION OF ELECTROLYTIC REFINING PROCESSES: ADVANCED MONITORING OF LIQUIDS WITH ED-XRF

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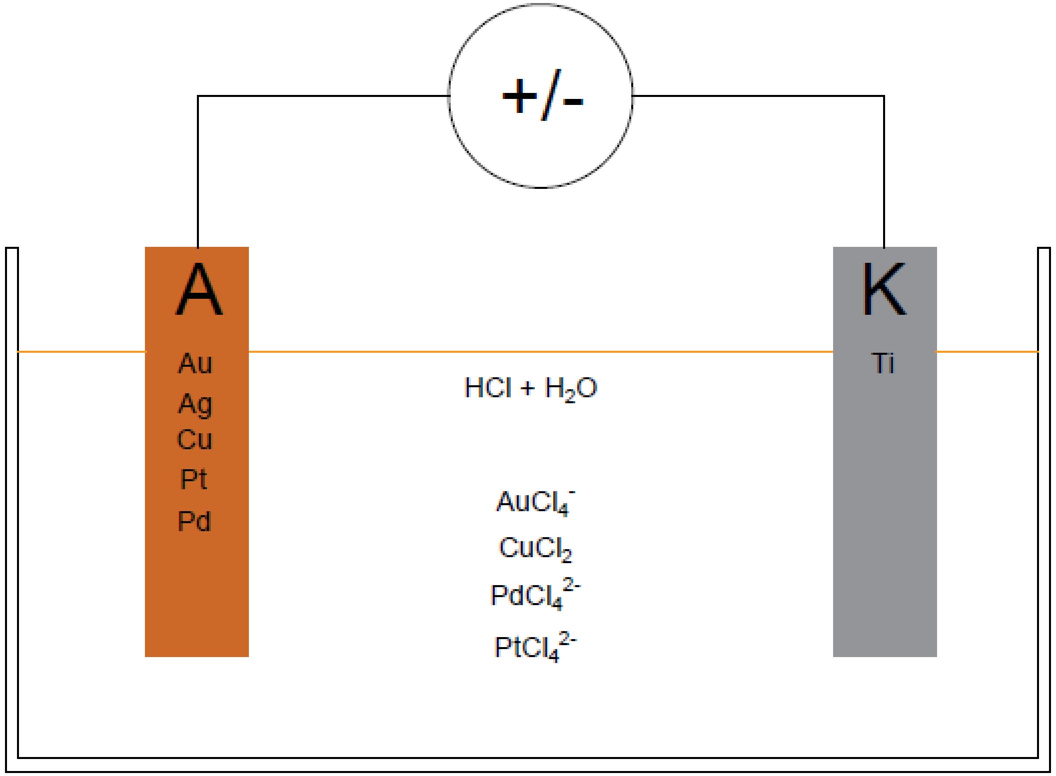
THE ELECTROLITYC REFINING



Anodic Reactions (oxidation):

Ag → Ag+ + e- E= - 0,80 V

Cu → Cu2+ + 2e- E= - 0,341 V

Pd → Pd2+ + 2e- E= - 0,95 V

Pt → Pt2+ + 2e- E= - 1,20 V

Au → Au3+ + 3e- E= - 1,498 V

2 Cl- → Cl2 + 2e- E= - 1,36 V

Cathodic reaction (reduction):

Au3+ + 3e- → Au E = 1,498 V

THE ELECTROLITYC REFINING

Chemical reactions:

$3Ag\ (s) + 4H^+\ (aq) + 3Cl^-\ (aq) + NO_3^-\ (aq) \rightarrow 3AgCl\ (s) + NO\ (g) + 2H_2O\ (l)$

$3Cu\ (s) + 8H^+\ (aq) + 6Cl^-\ (aq) + 2NO_3\ (aq) \rightarrow 3CuCl_2\ (aq) + 2NO\ (g) + 4H_2O\ (l)$

$Au\ (s) + 4H^+\ (aq) + 4Cl^-\ (aq) + NO_3^-\ (aq) \rightarrow AuCl_4^-\ (aq) + NO\ (g) + 2H_2O\ (l)$

$3Pd\ (s) + 8H^+\ (aq) + 12Cl^-\ (aq) + 2NO_3^-\ (aq) \rightarrow 3PdCl_4^{2-}\ (aq) + 2NO\ (g) + 4H_2O\ (l)$

$3Pt\ (s) + 8H^+\ (aq) + 12Cl^-\ (aq) + 2NO_3^-\ (aq) \rightarrow 3PdCl_4^{2-}\ (aq) + 2NO\ (g) + 4H_2O\ (l)$

The main influence in the success of the process, so in the quality of the final product, are:

- the optimization of the electric parameters
- the quality of the anode (generally from 700 to 990‰)
- the quality of the electrolytic solution

MONITORING OF THE ELECTROLYTIC SOLUTION

Preparation of the electrolytic solution:

$Au (s) + 4H^+ (aq) + 4Cl^- (aq) + NO_3^- (aq) \rightarrow AuCl_4^- (aq) + NO (g) + 2H_2O (l)$

The monitoring of the electrolytic solution is really important, sometimes is possible to choose the working plant depending on the quality of the anode, to increase the life of the solution, so reduce the consumption of reagents of the solution and to make the process more constant in the quality.

Is necessary to monitor the quantity of the contaminants as Pt, Pd and Cu, that can deposit on the cathode instead of gold and the quantity of the gold itself, to maintain a minimum quantity to foster the deposit.

MONITORING METHODS FOR REFINING BATHS

Potentiometry

High precision: Accurate measurement of specific ion concentrations.

Non-destructive: Does not alter the sample during analysis.

Versatility: Can be used for a wide range of analytes, including pH and specific ions.

Sensitivity to interferents: The presence of other ionic species can affect measurements.

Electrode maintenance: Electrodes require regular maintenance to ensure accurate measurements.

Coulometry

High sensitivity: Can detect very small amounts of analytes.

Quantitative: Provides precise measurements of the amount of electroactive substance.

Destructive: The sample is consumed during analysis.

Analysis time: Can take a long time to complete the electrolysis.

Amperometry

High sensitivity: Suitable for detecting low concentrations of analytes.

Speed: Provides results quickly.

Interferences: The presence of other electroactive species can affect results.

Electrode maintenance: Electrodes must be kept in good condition to ensure accuracy.

Electrogravimetry

High precision: Provides very accurate measurements of the amount of metal.

Quantitative: Directly determines the mass of the electrolytic deposit.

Analysis time: Can take a long time to complete the electrolysis.

Destructive: The sample is consumed during analysis.

Voltammetry

Versatility: Can be used for a wide range of analytes, including organic and inorganic compounds.

Detailed information: Provides both qualitative and quantitative data on redox reactions.

Complexity: Requires a good understanding of electrochemical techniques to interpret results.

Interferences: The presence of interfering species can complicate the analysis.

MONITORING METHODS FOR REFINING BATHS

ICP-OES

Method used before the introduction of ED-XRF
Radial view and cyclonic chamber

- **High-sensitivity:** possibility to detect also ppb of analytes.
- **Reduction of influence of interferences:** samples are really diluted and there are no problem related to interferer.

- **Time of analysis:** around 10 minutes for sample and calibration time. The times were decided by laboratory, not production.
- **Standards were not prepared in matrix** but starting from multielement solution.
- **Dilution of the sample:** related to the low range of linearity.

ED-XRF

Introduced from November 2024 in ARGOR-HERAEUS SA
50 keV and SDD detector

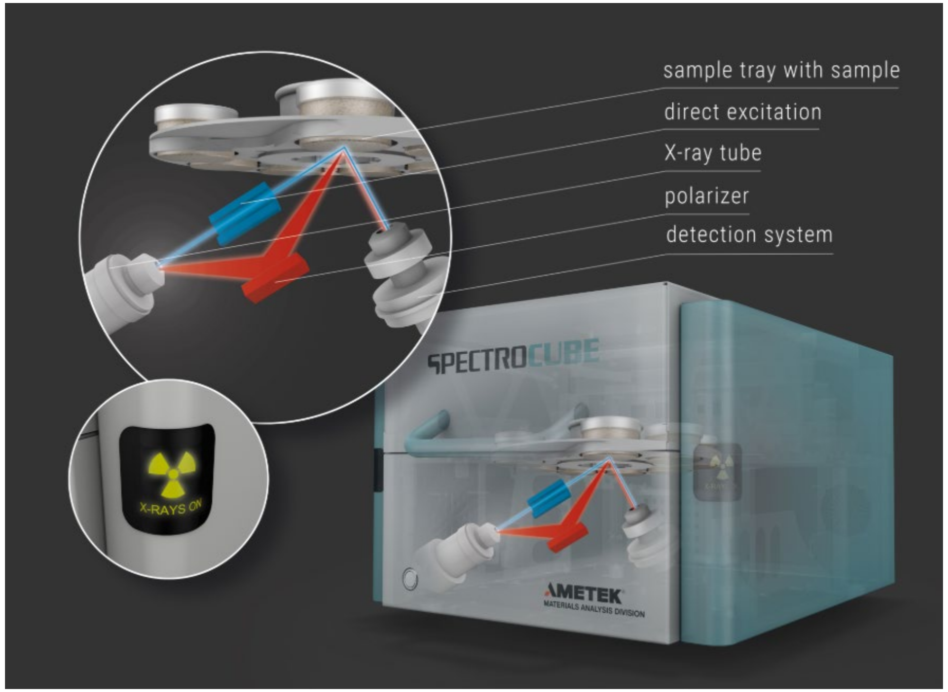
- **Fast:** time of analysis around 4 minutes and instrument in the production.
- **Possibility of analyse the sample as it is**
- **Good quantification of analytes:** possibility of quantification from ppm to %

- **Necessity of standards**
- **Necessity of the study of interferences**

ANALYSIS TROUGHT ED-XRF

ED-XRF is a very versatile analysis technique to analyse a variety of materials, avoiding the preparation of the samples, that sometimes is really complicated and time consuming.
This technique is useful when is necessary to analyse aqueous solutions, where the quantity of analytes stays in the range of percentage or ppm.

The SPECTROCUBE is equipped with adaptive excitation, which uses optimized excitation conditions for groups of elements including a polarized excitation when analysing elements in the range Na-Cl. This polarized excitation leads to higher sensitivity and lower scattered background in that spectral area and with this allows reaching low detection limits.



MATHEMATICAL MODEL

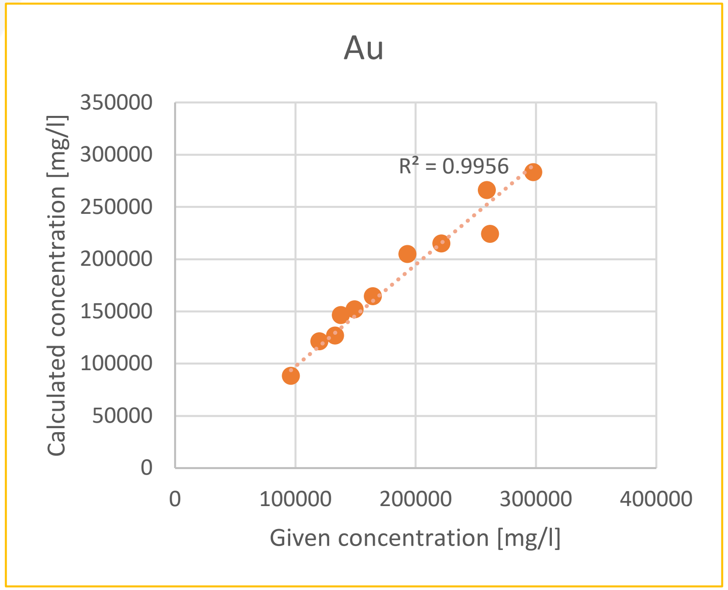
$$C_x = k0 + \frac{k1 * I_x}{I_{Compton}}$$

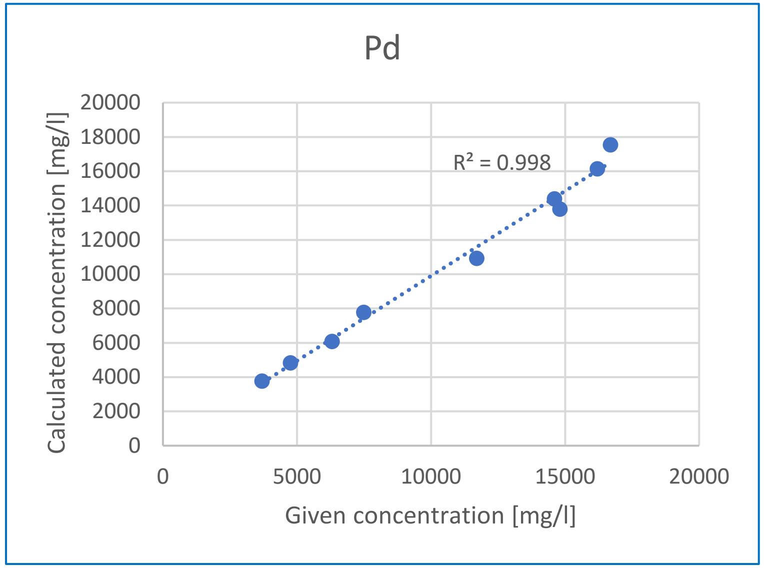
C_x: concentration of the element
$k0$: offset of the caibration
$k1$: calibration slope
I_x: fluorescence intensity of the element
$I_{Compton}$: intensity of the incoherent backscatter

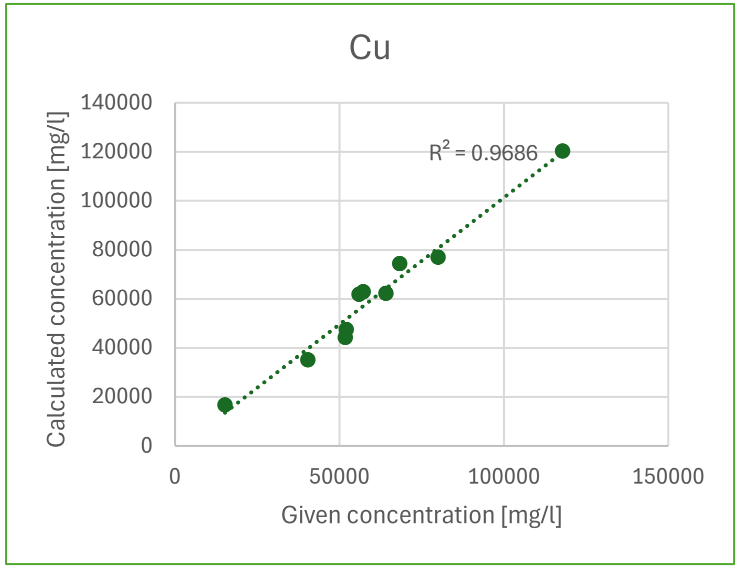
The mathematical model is the Compton, to obtain good results also if the matrix is slightly different, using a reasonable number of standards.
In this model the intensity of the element is corrected taking in to account the absorption effect on the backscatter intensity for the phenomenon where the monochromatic beam of X-rays strike an atom do not promote fluorescence, some energy can be bounced back to the detector as scattered radiation.

MATHEMATICAL MODEL

AMETEK ITALY







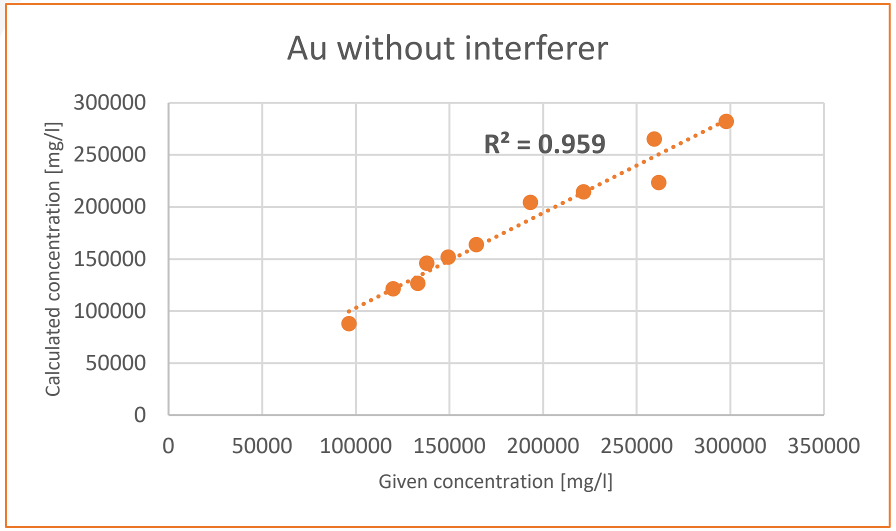
0,90 < R^2< 0,95 fair correlation

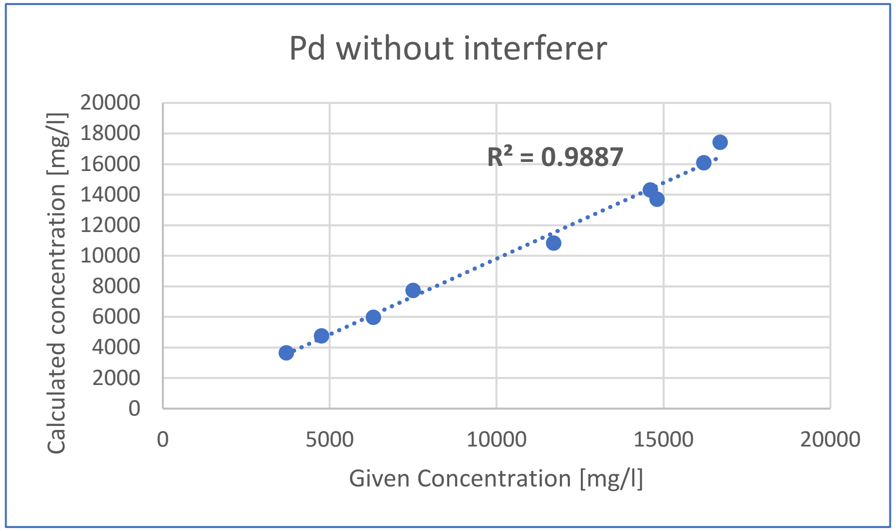
0,95 < R^2< 0,99 good correlation

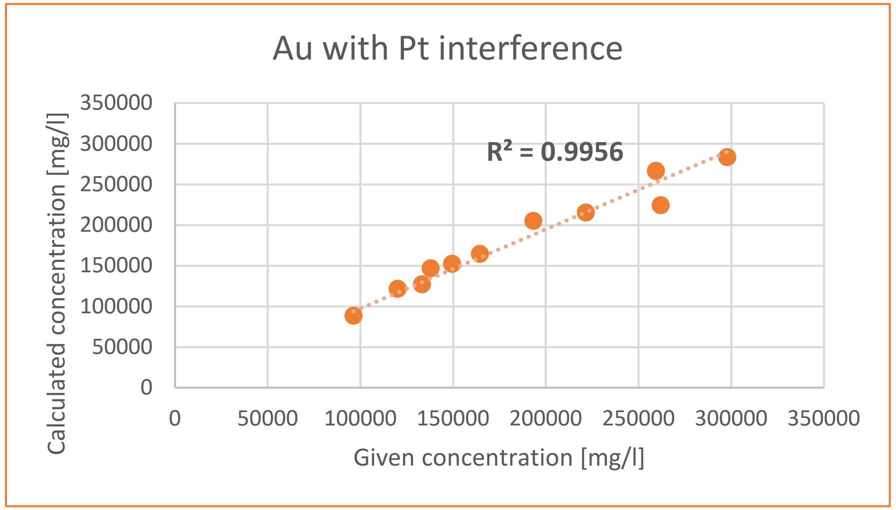
R^2> 0,99 excellent correlation

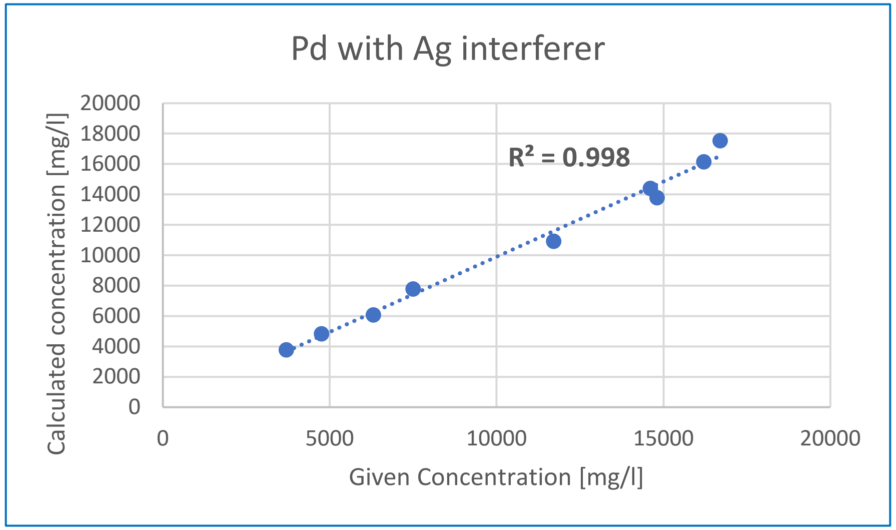
ARGOR-HERAEUS SPECTRO AMETEK

INTERFERER


Au without interferer
R² = 0.959
Calculated concentration [mg/l]
300000
250000
200000
150000
100000
50000
0
0
50000
100000
150000
200000
250000
300000
350000
Given concentration [mg/l]


Pd without interferer
R² = 0.9887
Calculated concentration [mg/l]
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
0
5000
10000
15000
20000
Given Concentration [mg/l]


Au with Pt interference
R² = 0.9956
Calculated concentration [mg/l]
350000
300000
250000
200000
150000
100000
50000
0
0
50000
100000
150000
200000
250000
300000
350000
Given concentration [mg/l]


Pd with Ag interferer
R² = 0.998
Calculated concentration [mg/l]
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
0
5000
10000
15000
20000
Given Concentration [mg/l]

COMPARING WITH ICP RESULTS

ICP data					SPECTROCUBE data				
	Au [mg/L]	Pt [mg/L]	Pd [mg/L]	Cu [mg/L]		Au [mg/L]	Pt [mg/L]	Pd [mg/L]	Cu [mg/L]
Banco 1	212245	770.751	18152.9	62742.7	Banco 1	220107	742.7	13740	64160
Banco 2	182753	1442.69	14185.1	63240.7	Banco 2	184112	1464	12380	63480
Banco 3	129669	335.968	3283.73	41629.3	Banco 3	148498	346.4	3518	42720
Banco 4	139218	800.395	8530.89	54875	Banco 4	142403	776.8	7492	55320
Banco 5	141372	1245.06	18053.8	63539.5	Banco 5	150298	1175	8976	60670
Banco 6	108603	889.328	2599.21	9660.39	Banco 6	127200	164.1	2540	1967
Banco 7	77052.2	474.308	15673	42924	Banco 7	71831	443	14750	32340
Banco 8	141465	227.273	2043.65	13743.6	Banco 8	174299	329.9	2423	8362

CONCLUSIONS

The benefits of the introduction of the SPECTROCUBE are that:

- Thank to the rapidity of the check, is possible to analyse directly the solution and intervene promptly, to improve the control on the quality of the final product.

- The analysis can be done directly in the production.

- The ability to quickly obtain information on the electrolyte, allows to choose the most suitable system for processing each anode batch. This allows the "life" of electrolyte solutions to be extended. In the long term, with the same quality of the anode charges, is expected a reduction in the volumes of "new" electrolyte and a decrease in the "exhausted" electrolyte to be processed for the recovery of precious metals.

- More control of the process and traceability of the product.

CONCLUSIONS

Here the comparison between the first weeks of 2024 (without monitoring with the ED-XRF) and the same weeks of the 2025 (after the introductions of the SPECTROCUBE).

2024-week	Au kg Aff	N banchi	KG NO CONF	KG NO CONF2
1	2914	15	0	0,00%
2	8060	39	700	8,68%
3	7348	36	100	1,36%
4	7426	34	0	0,00%
5	8650	36	0	0,00%
6	5580	25	300	5,38%
7	5942	25	0	0,00%

2025-week	Au kg Aff	N banchi	KG NO CONF	KG NO CONF2
1	0	0	0	0,00%
2	5066	26	0	0,00%
3	6438	33	300	4,66%
4	6122	27	0	0,00%
5	5446	25	0	0,00%
6	5381	24	0	0,00%
7	8814	40	0	0,00%

In conclusion on the 45920 kg of gold produced in the first weeks of 2024 results a nonconformity of the production of 2,4%, in 2025 on the 37267 kg was possible to reach a nonconformity of 0,8%.

THANK YOU FOR THE ATTENTION!

QUESTIONS?