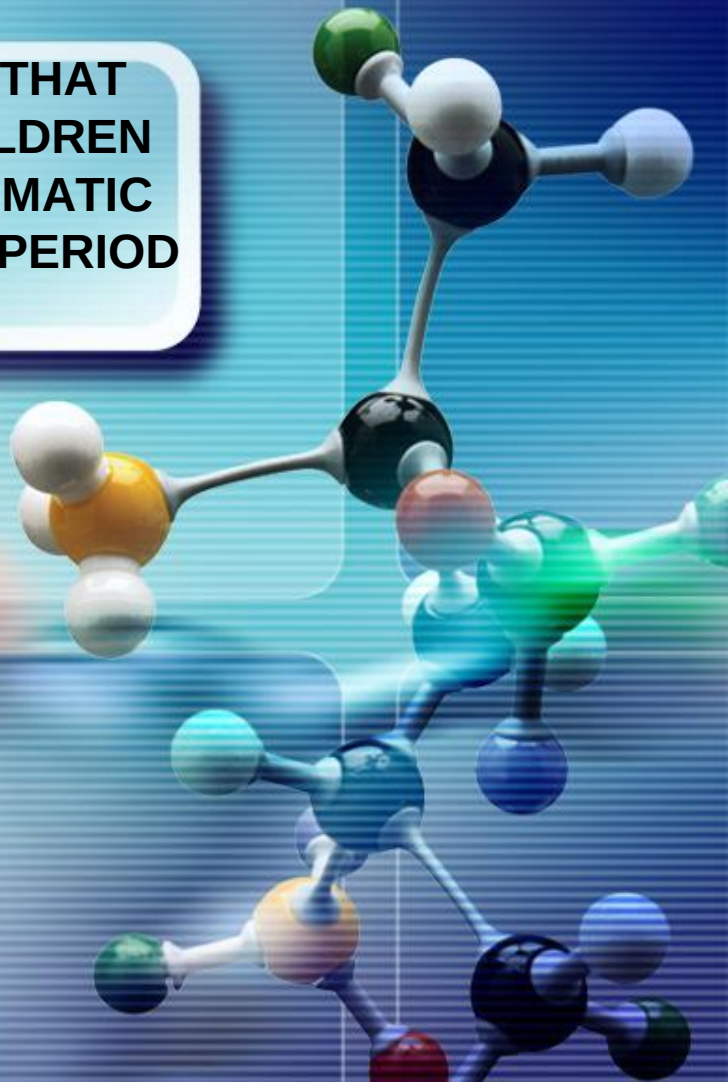
HEALTH SAFETY ON PLASTIC MATERIALS THAT COME INTO CONTACT WITH FOOD AND CHILDREN TOYS ABOUT MIGRATION OF PRIMARY AROMATIC AMINES (PAAs) EXAMINATION IN IPH- RM IN PERIOD 09.2011 – 06.2013

Institute for Public Health – Skopje

Republic of Macedonia



Introduction:

1. Humans can be exposed to PAAs by the usage synthetic products which come in contact with food. PAAs are suspected to be toxic and carcinogens.

2. PAAs are mainly originated from:

- synthetic azo dyes applied as colorants and
- from the use of adhesives based on polyurethanes (PU).

$$RNCO + H_2O = (RNHCOOH) = RNH_2 + CO_2$$

Introduction:

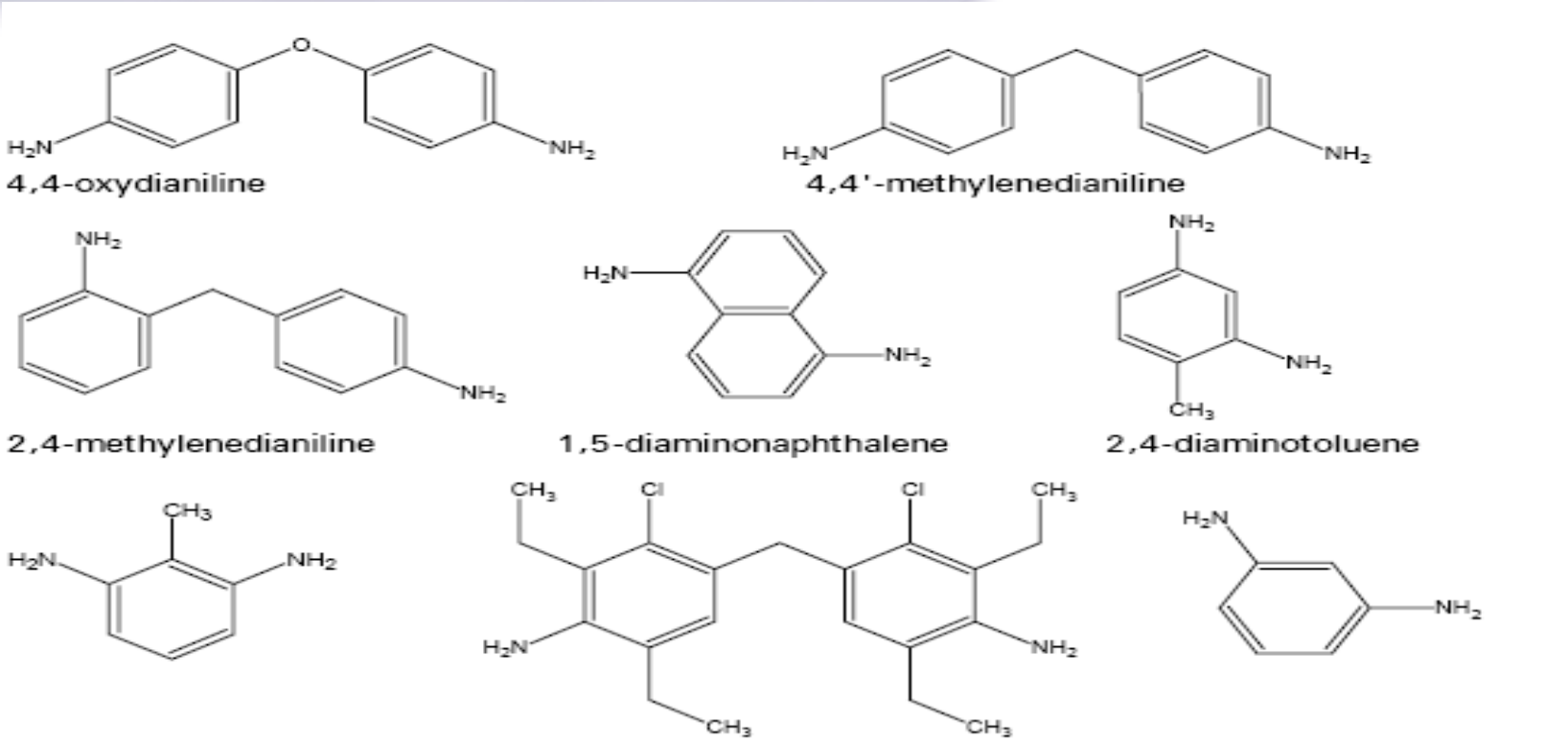


Figure 1. Important primary aromatic amines

Objective

Amines

Main objective:

- Establishing a spectrophotometric method with visible (Vis) detection, for quantitative determination of primary aromatic amines (PAA), expressed as aniline with optimization and validation of the proposed method.

- Determination of primary aromatic amines (PAA) in plastic items that come in contact with food and plastic toys in IPH RM- Skopje, in period 09.2011 – 06.2013.

MATERIAL AND METHODS

Amines

Materials:

1171 items: **557** - plastic toys and **614** were plastic containers, plastic utensils and plastic items that come in direct contact with food**.**

Apparatus and Laboratory Supplies:

- Spectrophotometer Lambda 12, Perkin Elmer, USA;
- Glass cells than 1 cm;
- Zucchini of 10 ml, 25 ml, 100 ml and 1000 ml;
- Pipettes from 1,0 ml; 2,0 ml, 5 ml and 10,0 ml (A-class);
- Electrical Scales Sartorius BP-110 S, Germany;
- Other laboratory equipment.

Reagents:

- Aniline hydrochloride ($C_6H_5NH_2$ x HCl) Sigma Aldrich, Germany;
- Chloride acid (HCl) pr.37%, pa Merck, Germany;
- Sodium nitrite ($NaNO_2$) pr:> 99%, pa Sigma Aldrich, Germany;
- Ammonium amidosulfonat ($NH_4SO_3NH_2$) pr:> 98%, Sigma Aldrich, Germany;
- N-(1-naphthyl) ethylenediamine dihydrochloride ($C_{10}H_7NHCH_2CH_2NH_2$ x 2HCl), pr:> 98%, Sigma Aldrich, Germany;
- Glacial acetic acid (CH_3COOH) pr. > 99,8%, pa Merck, Germany.

MATERIAL AND METHODS

Method:

Quantitative determination of sum of PAAs, expressed as aniline was made using spectrophotometric method based on diazotisation of PAAs and subsequent coupling of the obtained diazonium salts with N-(1-naphthyl) ethylenediamine dihydrochloride.

Made a modification of the spectrophotometric method (*Amtliche Sammlung von Untersuchungsverfahren nach § 35 LMBG, part 1/1, L 00.00-6, Beuth Berlag GmbH, Berlin, Koln, 1990*), so that it can be applied in rapid (screening) of total amount of PAA, expressed as aniline in simulant solution, not individually for each amine. Used a 1 M HCl and 0,5% $NaNO_2$, because PAA react in acidic medium nitritnite ions to form diazonium salts in the reaction with 1% N-(1-naphthyl) ethylenediamine dihydrochloride, form colored compounds with characteristic intense **violet coloration**, which intensity is proportional to the concentration of PAA in the test solution.

MATERIAL AND METHODS

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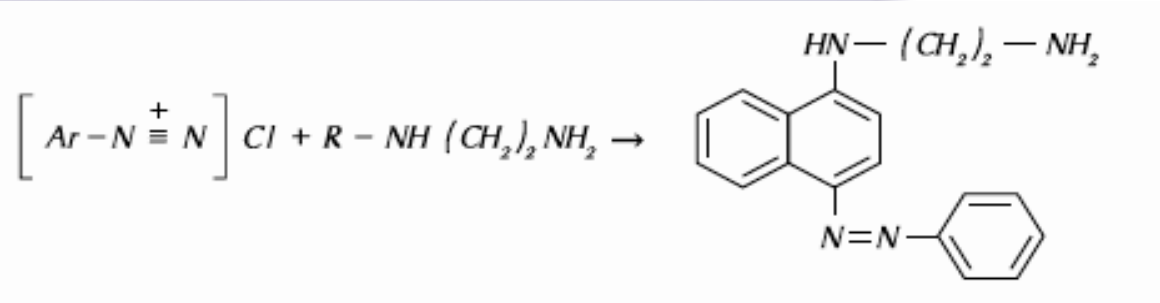


- The amount of PAA is calculated according to:

$$M_S = a \times c / 10 \times b = mg/dm^2$$

Where:

MS - specific migration of primary aromatic amines (expressed as aniline) in mg/dm^2.

a - apsorbtion/concentration of aniline hydrochloride/aniline, using a spectrophotometer.

b – surface of material or object in dm^2, which was in direct contact with the appropriate solution.

C - simulant volume of solution in ml.

Results and discussion

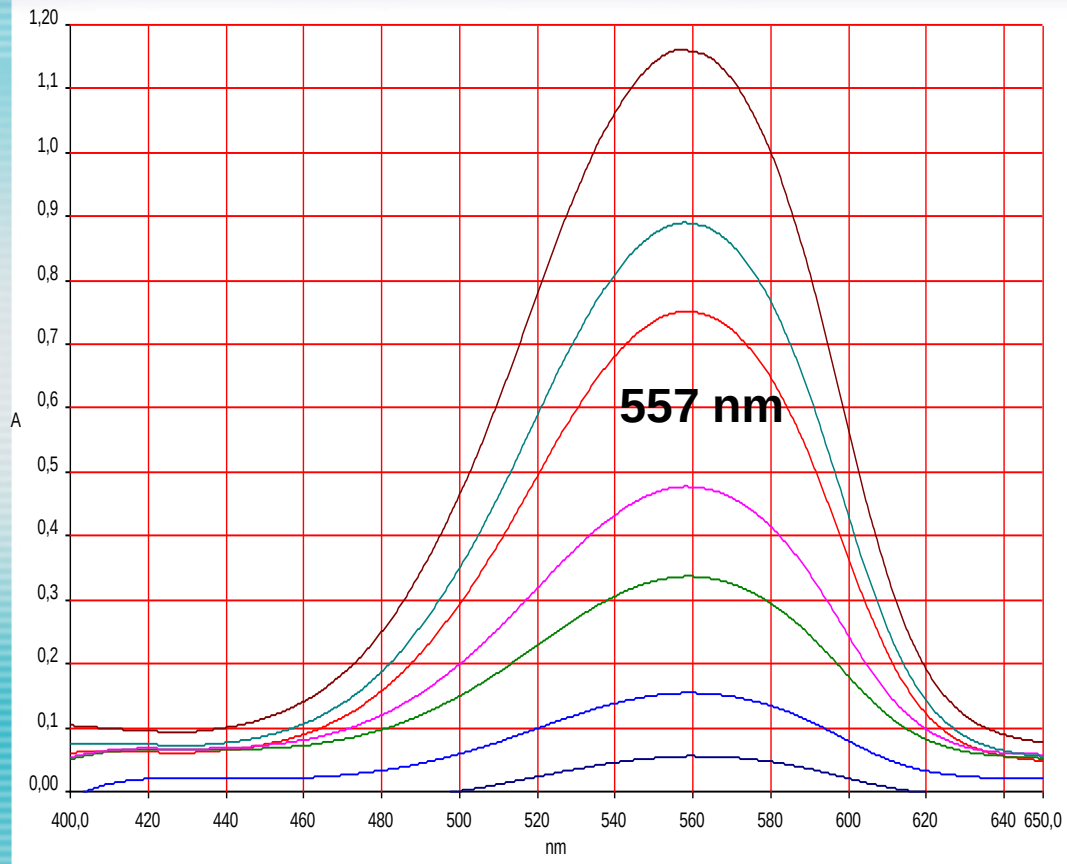


Figure 2. Wavelength of testing

Studies of PAA are made with pre-optimization method by applying:

- 3% acetic acid solution for as a simiulant immersion of samples;
- Certain temperature and time of extraction of PAA (2 hours at 70 º C and 10 days at a temperature of 22 º C);
- Spectrophotometric determination of wavelength of 557 nm

Results and discussion

Validation:

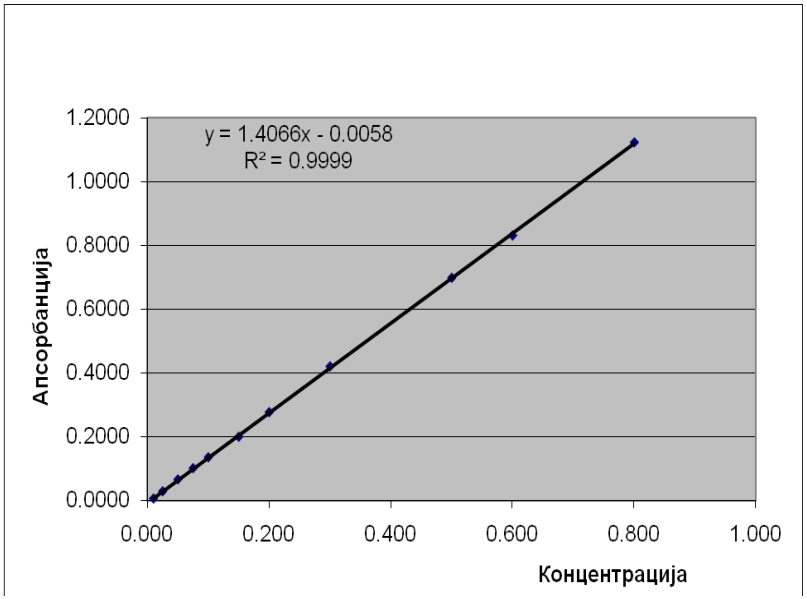


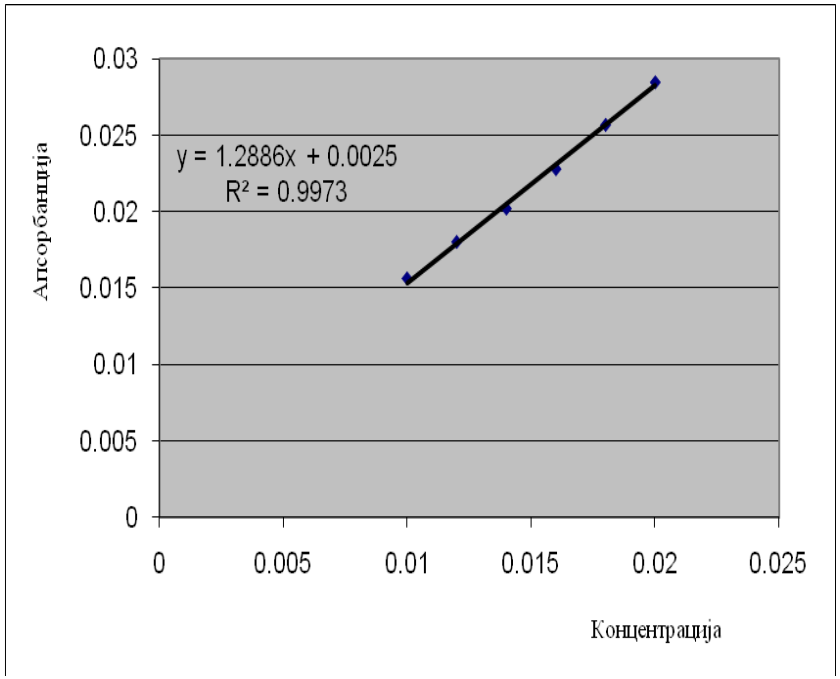
Figure 3. Calibration curve of aniline hydrochloride in 3% acetic acid

The calibration curve of aniline, obtained by the regression of rights presented in Figure 3, one can see that it is linear :

$y = 1.4066x - 0.0058, R^2 = 0,9999$

in the tested area of 0,01 mg/l to 0,8 mg/l.

Introduction:



The results of our tests for LoD and LoQ, the lowest concentration of aniline, which can be:
detected is 0,7 ng/ml, and the lowest concentration that can be **determined is 2,1 ng/ml**

Figure 4. Calibration curve standard solutions of aniline hydrochloride in 3% acetic acid concentrations: 0.01, 0.012, 0.014, 0.016, 0.018 and 0,02 mg/ l for determination of linearity and calculate the LoD and LoQ

Results and discussion

Figure 5. Items that come in direct contact with food and toys made of plastic

Results and discussion

Figure 6. Tested samples showing PAA value greater than maximum (0.01 mg/l)

Conclusion

1

Spectrophotometric method can be used for routine testing of primary aromatic amines in items made of plastics that come into direct contact with food and plastic toys, which is confirmed and the purpose of this labor

2

From tested 1171 samples about PAAs, expressed as aniline, only **24** exceeded DL = 0.01 mg/kg (*according to EU Regulation 10/2011*). From the faulty samples **18** were toys, and **6** sets coming in contact with food.

3

Requires increased sanitary inspection market, amid frequent occurrence of PAAs in plastic kitchen utensils, especially kitchen utensils in black and children toys made in China.

Thank You !