TED ANKARA COLLEGE FOUNDATION PRIVATE HIGH SCHOOL

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"THE EVERYWHERE CHEMICAL: PHTHALATE"

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ABSTRACT

This study is about a chemical that we are facing in every area of our lives but unaware of. This chemical is called “phthalate”. This study also contains significant information about the usage and the labelling of this material.

This chemical is known for its hazardous effect so the research question for this study is: *“What will be the effects of the phthalate and how do the producers label it?”.*

The reason why I selected this as my research question is that there was some very big news about some shoe companies that had excessive amounts of phthalate in the making of it. It caused several health problems and this situation made me question where do we also see this carcinogen chemical and the information that I have gathered was enough for crating an essay. I also learned about the environmental effects of this substance.

Phthalate is a substance which makes the plastics a bit more durable[1] to external factors. That’s why nearly every plastic on the market has a bit of phthalate in it. The usage of this chemical makes the plastic more efficient and better to use in everywhere of our lives. That’s why I wanted to title my essay as:

“THE EVERYWHERE CHEMICAL: PHTHALATE”

Word Count: 207

[1] *http://www.cdc.gov/nchs/data/nhanes/nhanes_11_12/phthte_g_met.pdf*

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I. INTRODUCTION TO EVERYWHERE CHEMICAL

There has been a growing need to find the effects of the chemicals we use in our daily lives to the wildlife, humans and the environment. From the researches that has been made some chemical substances showed some bad acts like ruining the endocrine system. Phthalate is one of them.

Phthalates are carcinogenic substances that are used nearly in every area of our daily life. They are generally used to make plastics more elastic, transparent and durable. The most common example for this transition is they are mixed with Polyvinyl chloride (PVC) to form the PVC we are using in our houses. It is known that this material is the most common chemical substance in plastic industry.

Although Phthalates are used nearly over 75 years, in the MEDCs (More Economically Developed Countries) researches has shown that this material is very dangerous for human health. In United States, Canada and EU (European Union) usage of this substance is limited and the companies who use this must use a code to show they use Phthalate. The USA National Toxicology Program made a research on mice with this substance and observed malignant tumor in the liver. They also stated that the mice also showed ruined testosterone. From these results the International Agency for Research on Cancer limited the usage of these substances.

There are much kind of Phthalates but the most used and dangerous one is DEHP also known as Diethylhexyl phthalate. Its formula is $C_6H_4(C_8H_{17}COO)_2$. It had the 54% of market share of plasticizers. It's a colorless liquid with oily

touch. It has an ester bond between phthalic acid and the branched-chain 2-ethylhexanol. It is one of the most used substances in the world as three billion kilograms of DEHP is used worldwide annually. In 1979 its known that the USA used 139 million kilograms od DEHP. DEHP has the same structure as DBP, DIDP and DINP (other phthalates), but it is much more sustainable and strong. Lastly is not soluble in water neither it can vaporize easily to atmosphere.

Due to its low cost it is highly used by companies as plasticizer to manufacture PVC. An average plastic bowl would have contained 3% to 42% of DEHP in it. It is also used in footwear, plastic packaging, medical devices, and electricity etc. Even in yoga balls, the pens we use, the Barbie dolls our little sisters are playing, and mostly in cosmetics (hair sprays, perfumes…).

Although the producer companies try to limit the danger the DEHP holds, they can't really manage to do it. It gets to environment and so to the world. Either you are a worker in the PVC factory or you are the consumer who just bought a new PVC product, you cannot escape.

Then what happens? After you are exposed to the dangerous world of DEHP. Children, especially adolescents, living near the producing factories can loose their ability to reproduce. They can be sterile. Moreover, women who are pregnant can go through spontaneous abortion. If not their newborn children may be result in lower IQ for a child. Adult exposure of it can result in cancer…

Carcinogen… How a material can be so bad for human health? That is the answer. DEHP is mostly known for his carcinogen effect and there are some regulations and so there are some regulations to the usage of it.

II. USAGE OF PHTHALATES

Starting from 1998 state of California, USA prohibited the usage of DEHP or any phthalate in plastic dolls[2]. In 2014 shoe sellers in Turkey bought products from China for a very good price. But they didn't know that these shoes contained DEHP more than any other plastic product. So the Turkish government confiscated these shoes and banned them. The European Union, with the lead of the French government, will ban the usage of DEHP in medical cares and this was held on the 1st of July 2015.

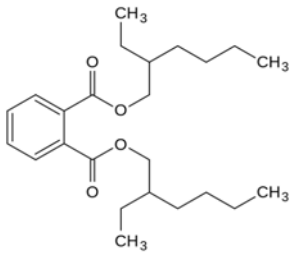
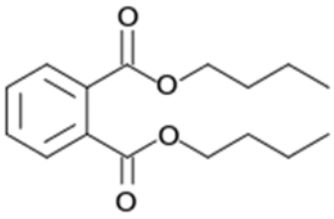
Another health issue that this product creates is that it is one of the reasons of diabetes type-II. This sperm lowering products also causes obesity. The higher DEHP level in your blood, the more chance you would be obese and have high BSL (Blood Sugar Level).

DEHP also caused some national disasters. The most known and common one is in Taiwan, 2011. It is also known as *2011 Taiwan food scandal.* The absolutely scandalous occurrence was, they used DEHP instead of palm oil as clouding agents in fruit juices. Palm oil is way more expensive than DEHP and they give nearly the same results as clouding agents. Clouding agents are products that are used in fruit juices to make them look more natural and come up to a level of fluidity. For that reason, the international markets in China, Hong Kong, USA etc. banned these Taiwan products from their shelves. But the

[2] *http://www.knauer.net/fileadmin/user_upload/produkte/files/Dokumente/application_notes/vev0004n_phthalates_by_hplc.pdf*

Taiwanese government could not cope with the production so by 2013 the fruit juices with DEHP were on the shelves again. Although USA limited the usage of DEHP in plastic dolls the risk of the American children stands as the factories produce millions of dolls for the children every single day.

Table 1: Identifying of the most common Phthalates.

NAME (IUPAC/COMMON)	**Bis(2-ethylhexyl) phthalate DEHP**	**Dibutyl phthalate DBP**
FORMULA	$C_{24}H_{38}O_4$	$C_{16}H_{22}O_4$
MOLECULAR SHAPE		
MOLAR MASS	390.56 g·mol−1	278.35 $gmol^{-1}$

The general molecular structure of the phthalates is shown in figure 1 below.

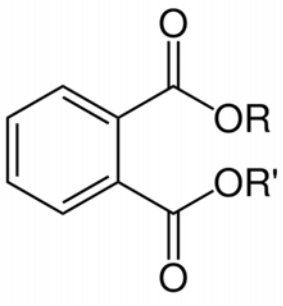


Figure 1: General molecular structure of phthalates as the R and R' are radicals

Phthalates require a benzene cycle and two radicals at the end. Its oxygen are also attached the carbon with one sigma and one pi bond.

If I had to talk about the properties of the molecular structure of both plasticizers, DEHP is more complex than the DBP as it has different and longer branched radicals. It also is heavier 112.21 $gmol^{-1}$ than the DBP.

DEHP is a colorless, oily liquid which has the melting point of -55^0C and boiling point of 230^0C. It nearly has the same density as water with 0.98. Its estimated that this substance has more than 50% of the market share in the plasticizers world. Considering Annex of Council Directive: Human Health it is toxic to reproduction.

The other important phthalate in this thesis is DBP as said. Although they, DEHP and DBP, have branched side chains DBP's has a shorter one. It has the melting point of -35^0C and has the boiling point of 340^0C. It has the density of 1.045 and it is also classified as a cause to unborn child, risk of impaired fertility and dangerous to environment, especially aquatic ones. It has the market share of 5% among the plasticizers.

Phthalates are used in substances that demand high performance, long-last and durable. The industry that involves phthalate in it has an estimated value of 35 billion dollars. Their isolative property causes them to being used the wires to protect them. Their durability to extreme heats make them suitable for them to

being used in hospitals and interior side of our houses. For the outside they are brilliant dye holders.

With the great usage comes great responsibility for governments to look out for troubles. The United States National Toxicology Program's Center for Evaluation of Risks to Human Reproduction stated their minimal concerns in this issue as the sperms lost their ability to move when they are exposed to too much phthalate. So this made the government took action so they specified the chemicals and worked on the lowering of the usage in the industry. Actually this was a successful act as the exposure is lowered in the 10 years after.

Professionals recommend people to use metal, or any non-plastic material to store their food. They also say don't buy any plastic toys to your children and look for the code "3" which shown the credible PVC that you can use and recycle.

PVC are used in every area of our lives. It is often used with DEHP and that brings cancer right into our food pyramid. Not just foods, plastic bottles, windows, soaps, etc. These aspects of phthalates caused us human beings to measure the analytical observation of phthalates.

They wouldn't create or make any reactions with low reactive polymers. That's why when they are mixed with the base of our daily life in the chemical basis, polymers, and thrown away with excessive ones, they do not solute in water. They get directly into the ecosystem.

III. LABELING OF THE PHTHALATE

United States Consumer Product Safety Commission Directorate for Laboratory Sciences of Chemistry [3] set a necessary analytical analysis of standardized phthalate content in children's toys. Protection of the children is the prior aim to this analysis. The general Approach was to dissolve the sample completely in tetrahydrofloran (THF) and precipitate the PVC with hexane. Moreover, filter and dilute the solution with cyclohexane and analyze the phthalates with Gas Chromatography-Mass Spectrometry (GC-MS).

The GC-MS method is used for to identify different chemicals within a sample. It monitors and traces the corresponding ions and shows the time of the substances that were found in the substance we are testing. This monitoring helps us to determine if the corresponding substance is organic, inorganic or biologic.

To try this method to analyze phthalate content in toys you need the corresponding equipment:

1. Tetrahydrofuran (THF, C_6H_8O)
2. Hexane (C6H14)
3. Cyclohexane (C6H14)
4. Sealable glass vials with polietrafloroetilen (PTFE) cover inside (20 mL)
5. Cryogenic-mill
6. PTFE filters

[3] *https://www.cpsc.gov/PageFiles/126591/CPSC-CH-C1001-09.3.pdf*

7. GS-MS with auto sampler and capable of selective ion monitoring
8. Phthalate content (Toys, leathers, etc.)

The determination of phthalate content in toys consists of three sections. These are:

1. Sample preparation
2. Extraction
3. Analysis

Before getting into action you must know that that these methods require the use of hazardous materials. Phthalates are also highly contaminant. Even low levels of contact can impact the results. That's why the usage if PTFE is very important in this experiment as it avoids the contact between the phthalate and the glassware.

Before getting into the sample preparation section, there is also an optional section which is called "Sample Pre-Screen Using Infrared Spectroscopy". In this section the sample is observed between the 1580-1600 wavenumbers (cm^{-1}) and the founded data can be used to dilute the sample.

a. Sample Preparation

Before starting anything in chemistry you must have something to test. A sample is a product batch to be tested in an experiment. In this experiment you would have to cut the plastic toy or leather into $2mm^2$ so that you can minimize the sample area. After the cutting of these samples, you must pulverize. Do that till you get a sufficient amount of sample size. The higher the surface are, the better it will dilute.

b. Extraction of Phthalate

Extraction of a phthalate is not easy as its insoluble in water. So you need to follow this method below:

1. Weigh minimum 0.05 g (± 0.005 g) of sample into sealable glass.
2. Add 5 mL of THF to the sample. Then shake, stir or optionally mix the solution for at least 30 minutes. You can heat the sample up to expedite dissolution.
3. Precipitate any PVC with 10 mL of hexane. Wait about 5 minutes for polymer to settle.
4. Filter the THF-Hexane solution with PTFE filters.
5. From the filtered solution take 0.3 mL and 0.2 mL from internal standard (which is in this case Benzyl Benzoate, $C_6H_{12}O_2$, BB)
6. Dilute it to 1.5 mL with cyclohexane.

Before getting into the operating of GC-MS you must consider the operating system of the machine. You must know what you are looking for and what you need to do to find that answer.

Table 2: GC-MS Conditions

Flow Mode	1 ml/minutes, constant flow (He gas)
Inlet Mode	20:1 Split or Splitless
Injection Amount	1 μl
Inlet Temperature	290^0C
Solvent Delay	5 minutes
Initial Oven Temp, Hold Time	50^0C, 1 minutes

Ramp 1	30^0C/minutes, 280^0C
Ramp 2	15^0C/minutes, 310^0C
Final hold time	4 minutes or longer

Table 3: Corresponding ions

	Estimated Retention Time	**Corresponding Ions (m/z)**
DBP (Dibutyl phthalate)	8.5 minutes	223
DEHP (Diethylhexyl phthalate)	10.4 minutes	279

b.1. Working Mechanism of the GC-MS

Gas Chromatography-Mass Spectrometry device is combination of two devices. Gas Chromatography and Mass Spectrometry. These two types of chemical analysis combine to an effective analysis of chemicals in the same objects. It can be called a confirmation test too. Its generally used in the analysis of drugs and performance enhancing pills and chemicals.

b.1.1. First Part: Gas Chromatography

The first step in the GC-MS machine is gas chromatography. Its basic principle is to vaporize and analyze the every different chemical in a substance or simply the sample we examine. Different characters of chemicals show peaks at the chromatograph. The time of the retention of that substance is called retention

time and its significant for every different molecule. It separates the different chemicals in the same sample by just vaporizing.

There some things to be considered in this procedure as the usage of a gas. This gas flows and helps the sample to vaporize. These gases should be noble gases as they could effect the statistical data. The usage of noble gas is important as they don't react with any substance meaning that they don't take a significant role in the calculations. This concludes us to reliable results which is our aim. Its also important to use non sticky materials as some particles may stick to syringes and that small amounts of particles effect the results. Finally, its also important to use a calibrated device.

b.1.2. Second Part: Mass Spectrometry

This method of chemical analysis is used to quantitate the known material in a sample. It identifies unknown components in samples. It clears out the structure and chemical properties of significant molecules.

It runs with four steps. Ionization, acceleration, deflection and then detection. The first step is to turn the sample into gaseous ions by electron ionization. After that these ions go through a fragmentation. After fragmentation separates the ions to their specific mass to charge ratio (m/z).

It studies the effect of ionization energy. One of the main principles can be elucidated by a simple example. Think of an atom going through a straight line. If that atom encounters with a magnetic force the atom moves in a curve, it deflects. It extracts force sideways. The mass is an important aspect in this occurrence as the mass of the atomic mass increase the deflection decreases.

c. Analysis

After all these preparations, comes the analysis part. Now that the mechanism which is GC/MS is know and the sample is extracted. This procedure generally runs in the splitless mode which is stated in table 2.

1. Prepare the calibrated GC/MS
2. Analyze the samples in both blank and full scan mode both in GC/MS and Simple Ion Monitoring(SIM).

SIM: A gas chromatography/mass spectrometry full scan will monitor the distribution of the mass ratio in the substance whereas the SIM targets one ion and specifies the substance. It makes the scientific reliability increase by 1000%.

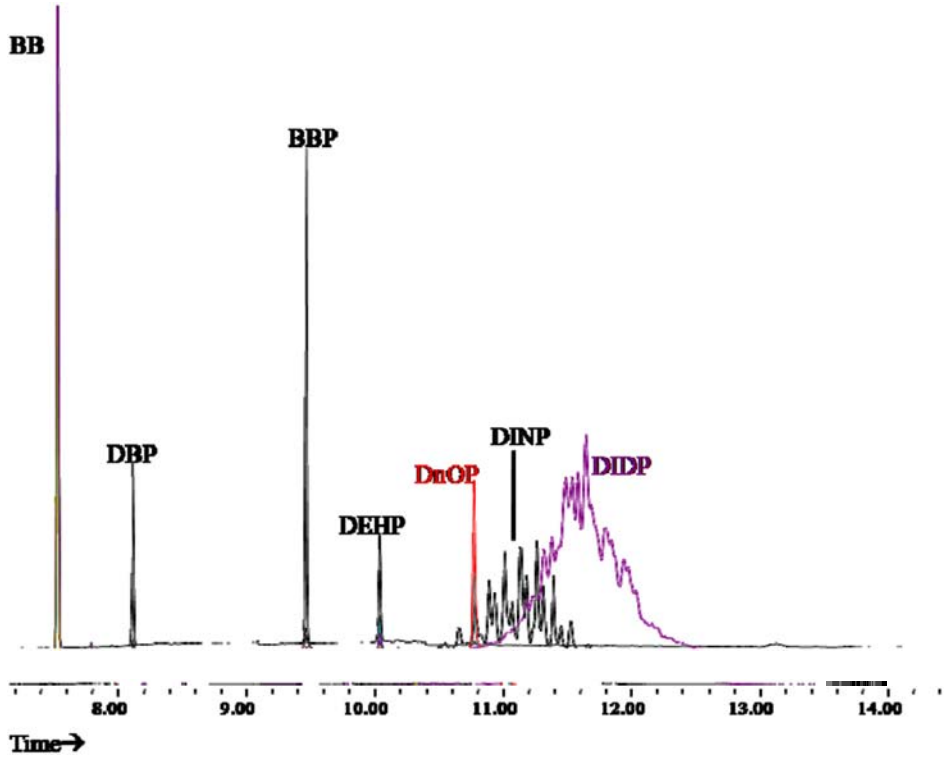
3. Create an expected curve by using the following formula:

$$Pht_n = \frac{\mathbf{Pht}}{\mathbf{ISTD}}$$

Pht phthalate response **/ ISTD** internal standard response

4. Calculate the data. It it is not in the range of 15% of the expected value, prepare new batch and re-run the calibration.
5. Evaluate full-scan results. Phthalates should be identified by matching retention times.
6. Evaluate the SIM results. Again, if it is out of the range, return to the phthalate extraction method and perform another dilution. If it doesn't work again inject a bit more in to the GC/MS but do the calculations accordingly.

Figure 2. Chromatogram overlay of all phthalates of interest and internal standard.



d. Calculations

Calculations of the concentration of any phthalate is made by the help of this formula:

$$\text{Percentage Phthalate \% (w/w)} = \frac{\mathbf{C \times V \times D}}{\mathbf{W \times 1000}} \times \mathbf{100}$$

C *Concentration of phthalate in GC/MS* ***/ V*** *total volume of hexane+THF added*

D *Dilution Factor* ***/ W*** *weight of the sample collected*

To give a conclusion set and a bit more understanding to this thesis I will now try to explain what I have said with a made experiment. So to have all things remembered:

1. A plastic toy was cut into small pieces and then powdered.
2. 50 milligrams of the batch is taken and dissolved in 5 milliliters of THF.
3. After that 10 mL of hexane is added to the solution.
4. From the solution 0.3 mL was taken and it was made to be combine with 0.2 internal standard and added cyclohexane till the total amount reached 1.5 mL.
5. The solution was injected to GC/MS and the found data was like this:

Table 4: Measured amount of DEHP in a PVC plastic toy

	Measured DEHP Concentration (μg/mL)	**Original Volume of the Solution (THF+Hexane) (mL)**	**Dilution Factor (Solution/Taken Amount)**	**% DEHP (w/w)**
Toy 1	350	15	5	52.5
Toy 2	150	15	5	22.5
Toy 3	175	15	5	26.25
Toy 4	150	15	5	22.5
Toy 5	230	15	5	34.5

From these calculations I can say that the naïve looking toys that every child have are not that naïve. They show different variety of DEHP

concentrations. These toys should be tested and prohibited before they reach to our homes. Instead we should seek for healthy organic plastics.

IV. CONCLUSION

The usage of the chemistry has become so common that in the 21st century one of the most increasing industry is the “Chemical Industry and Engineering”. In this industry the products are distributed by three tenth of the products are pure chemicals. For example, detergents, soaps…

The other seventy per cent of the chemicals produced in this industry is used as monomers in other industries. They are the base of the general industry in the world. Just like phthalates chemicals are everywhere we see in our world, but we are not aware of them.

Four percent of the worlds money comes from textile industry. In this thesis the term chemical is used for both a specific substance defined by CAS (Chemical Abstract Service) and for a mixture of chemical substances. In this case a textile chemical can be defined as the chemicals directly involved in any part of the production of the textile creation cycle.

In textile a fabric can be seen as a monomer as it is the base of all our clothes. A fabric, at least, has 27% by weight chemical in it. To add to produce one kilogram of fabric, you would have need about between 1.5 to 6.9 kilograms of chemicals due to its quality. As a matter of fact these carcinogen substances which are used to make the fabric more qualified are in direct touch with our skin. This fact causes some real problems to both us, humans and the environment itself.

To give an example for this, in late 2014 five containers of shoes imported from China to Turkey has entered. There were exactly 25,510 shoes in those containers. The shoes were subjected to phthalate tests and they were not permitted to be sold in Turkish market. However, it was too late because it took about 33,000 shoes sold before this incident. These “Hazardous Shoes” held a great place in Turkish media and caused lots of wounds in the customers’ foots.

The substance that caused this was not phthalate. It was “azo paint”. This material was used to create fashionable and fresh dyes. To make the paint more durable phthalates are used. REACH actually prohibited the usage of azo paint till it was found to cause bladder cancer.

To prohibit any further Turkish Government now makes the testing of phthalate testing obligatory in the customs. Governments need to make these kind of laws as the manufacturer doesn’t necessarily need to clarify the phthalate amount in any of the material produced. This causes to laboratories to be set up in customs.

To have all things considered in this thesis, phthalates used as plasticizers are in everywhere of our life. Hospitals, cars, pens, windows and even maybe the most naïve entertainment system for our young brothers and sister, toys… They are used to make the plastic softer. They make any substance they are used with durable, resistant to different weather conditions and extreme heats. That’s why it wouldn’t be fair for any of us to say “Companies shouldn’t use this chemical.”. They do. But we are not aware of the toxicity of this chemical.

If I had to summarize the phthalates with just one on two words, it would be “Everywhere Chemical”. This everywhere chemical causes lots of troubles not just us human beings but also the environment as they are not soluble in water and nearly has the same physical properties under the same conditions. This everywhere chemical is trying to be controlled by governments and they made a great job in ten years.

Finally, I would like to define chemistry as the art of change, because in chemistry everything we know has the ability to change very quickly. This change sometimes is so rapid that we don’t know what is happening. This makes one of the most used chemicals a chemical of everywhere.

BIBLIOGRAPHY

1. Gordon, J. J., E. Weiss, O. K. Abayomi, J. V. Siebers, and N. Dogan. "The Effect of Uterine Motion and Uterine Margins on Target and Normal Tissue Doses in Intensity Modulated Radiation Therapy of Cervical Cancer." Physics in Medicine and Biology Phys. Med. Biol. 56.10 (2011): 2887-901. Web. *http://publications.jrc.ec.europa.eu/repository/bitstream/JRC76656/lb_na_25674_en_n.pdf*
2. "Standard Operating Procedure." SpringerReference (n.d.): n. pag. Web. *https://www.cpsc.gov/PageFiles/126591/CPSC-CH-C1001-09.3.pdf*
3. Han, Wenning. Analytical Challenges in Detecting Regulated Phthalates in Flexible PVC Products (n.d.): n. pag. Web. *http://www.plasticsindustry.org/files/events/Wenning%20Han_Tuesday.pdf*
4. Clerici, Lisa. Using Dual Instrumentation for Phthalate Analysis (n.d.): n. pag. Web. *http://www.cpsc.gov/PageFiles/127217/clerici03012012.pdf*
5. GAFTI Analytical Method for CPSC – Detection and Determination of Phthalates in Prints by GC/LC-MS (n.d.): n. pag. Web. *https://www.wewear.org/assets/1/7/GAFTI_Phthalates_SOP.pdf*
6. Adewuyi, G.O. and R.A. Olowu. 2012. “High Performance Liquid Chromatographic (HPLC) Method for Comparison of Levels of some Phthalate Esters in Children’s Toys and Their Health Implications”. Pacific Journal of Science and Technology. 13(2):251-260.

http://www.akamaiuniversity.us/PJST13_2_251.pdf

7. Marten, Silvia, and Mareike Naguschewski. Application Note. Berlin: KNAUER, n.d. Web. http://www.knauer.net/fileadmin/user_upload/produkte/files/Dokumente/application_notes/vev0004n_phthalates_by_hplc.pdf

8. Kho, Young Lim, Ji Yeon Jung, Kyungho Choi, and Pan Gyi Kim. "Daily Intake of DEHP and Other Phthalates by Korean—-Estimated by Determination of Urinary Concentration of Phthalate Metabolites."Epidemiology 22 (2011): n. pag. Web. http://www.cdc.gov/nchs/data/nhanes/nhanes_11_12/phthte_g_met.pdf

9. Karakaya, Asuman, and Nevin Vural. "Gıda Ambalajı Olarak Kullanılan PVC Plastik Malzemelerde Ftalatların Gaz Sıvı Kromatografisi-ECD Yöntemi Ile Tayini." Ankara Universitesi Eczacilik Fakultesi Dergisi (1987): 024-32. Web. http://dergiler.ankara.edu.tr/dergiler/24/978/11999.pdf

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