Novel design and implementation extraction $^{137}$Cs from seawater integrated with water quality checker

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Abstract. The main source of $^{137}$Cs radioactive releases categorized as global fallout came from nuclear weapon experiments in the past as well as nuclear accidents of the Chernobyl and Fukushima nuclear power plant that occurred in 1986 and 2011. Radioactive contamination in the atmosphere will be deposited on land and dispersed through the water. The existing operational nuclear facilities and government plan to construct an Experimental Power Reactor in the Serpong Puspitek area could potentially release radioactive $^{137}$Cs through the Cisadane river towards into Jakarta Bay. Environmental monitoring of fission products is required to control the level of radioactivity of the marine environment when the new nuclear facilities and existing facilities operate. On the other hand, the old unit has a weakness of adsorption efficiency and suspected not perfectly coated in filter cartridges. Compared with the old design, this unit easily mobilized and integrated with the measurement of seawater parameters refers to pH, conductivity, and temperature. This unit fulfilled IAEA analytical guidelines with the results of decision threshold and detection limit were 0.13 mBq/l and 0.29 mBq/l respectively, also the results of the relative bias and precision test are below the permissible limit.

1. Introduction

The main source of radioactive release $^{137}$Cs are categorized as a global fallout from nuclear weapon testing in early 1950s as well as the release from the Chernobyl and Fukushima nuclear power plant, which were reported in 1986 and 2011 respectively [1,2]. The radioactive contamination in the atmosphere will be deposited and dispersed through the ocean. Due to their chemical properties, the $^{137}$Cs radionuclides can be soluble in seawater, which allows them to spread over long distances and dispersed to various territorial waters by marine currents [3,4]. The radiocesium potentially entered the Indonesian waters through the oceanic water mass, as a consequence of geographical location between Pacific Ocean and Indian Ocean [5]. Identical comparison of T-S graph from monitoring data in the Lombok strait and Pacific ocean was implies the sources [6].

At present the government plans to build and operate an Experimental Power Reactor (RDE) which aims to gain experience and expertise in terms of operating nuclear reactors. Existing nuclear facilities operations and RDE development plans in the Puspiptek Serpong area can potentially release radioactive $^{137}$Cs through the Cisadane Rivers run out into the Jakarta Bay. The environmental monitoring of radioactive content in fission products is needed as a control of the level of radioactivity...
of the marine environment when planned nuclear facilities and existing facilities operate. The marine water environment monitoring program has been carried out limitedly in several Indonesian marine waters. The baseline data is very important for nuclear power plant development as well as to anticipate the possible impact of nuclear accidents such as in Fukushima on Indonesian marine waters [7].

On the other hand the concentration of $^{137}$Cs in the ocean is very small between $(2.9-6.5) \times 10^{-9}$ M [8]. The present of cesium radionuclides in very large volume of seawater are combine with concentrations of sodium, magnesium, calcium, chloride, sulfate and bicarbonate [8]. Based on that proportion of radiocesium, seawater sampling requires a very large volume in order to analysis with concentrations above the limit detection of instrument.

The easiest method to determine cesium in seawater is using hexacyanoferrate ion exchanger because it does not required acidified pH and less laboratory work. However, it requires a long process and requires a large volume (about 200 liters) [9], this method were simple for monitoring large volumes of waters where low detection limits are required [10]. Earlier seawater sampling had been done through manual measurements in conventional system and need huge container include treatment in field [7, 11, 12]. This method had been developed by making new prototypes that are assembled with microcontroller, sensors and data recorders.

2. Experimental
2.1. Design prototype
The prototype hardware was designed solid, compact and easy to mobilize in the sampling site. This system using a single chip ATmega2560 microcontroller as a processor base on arduino. The main part of the system are showed in the figure 1 consist of front panel display, chamber sensors as the place for the sensors, cartridge housing for hexacyanoferrate filter and flow meter to measure flow rate and volume of seawater. The data will showed in LCD and stored in SD card that can reopened on a PC.

![Figure 1. Block diagram of the prototype for extraction $^{137}$cesium in seawater using cartridge filter hexacyanoferrate](image1)

![Figure 2. Overall system look of the prototype](image2)

![Figure 3. Display and interface of prototype](image3)
Figure 1 describe the flow of water pump trough the flow sensor and divided into two line. First, the flow goes directly to the cartridge filter, the second flow to the sensor chamber for measurement and will be displayed on the LCD. This method can apply in close loop using huge container of seawater or open loop using circulated seawater directly from the sea. The solenoid valve on the block diagram indicates this system can run in static and dynamic measurements. That was mounted the level sensors will activate the solenoid valve to close or open.

2.1.1 Flow sensor. Previously this system used an analog flow meter that displayed readings of measurement results came from the pointer and numeric displays that were mechanically connected to the shaft. In this prototype using OF05ZAT with simple structure due to the elliptic gears employed as a measuring principle that can be used to measure the micro flow. The flow meter consist of magnetic sensor, which is strong against noise and output is proportion to the velocity.

2.1.2 pH sensor. An industrial pH sensor by DF Robot was installed on this prototype using BNC connector and PH2.0 sensor interface. The output voltage of the electrode is linear in 0 to 14pH range, The Ag/AgCl gel electrolyte salt bridge as reference sensor has a stable performance and suitable for long-term monitoring.

2.1.3 Conductivity sensor. An analog electrical conductivity by DFRobot was used to measure the electrical conductivity of seawater. It supports 3-5v wide voltage input, and compatible with 5V and 3.3V main control board using BNC connector. The output signal is filtered by hardware and has low jitter.

2.1.4 Temperature sensor. A linear temperature sensor LM35 produced by National Semiconductor Corporation was mounted coincide with the pH and Conductivity electrode. Functionally its sensor can working in range between 0 to 150 °C. The output sensitivity was 10mV/1°C and proportional to the temperature.

2.1.5 DC water pump. The simplest type of motor pump is the brushed DC motor. In this type of motor (model:JT-600), electrical current is passed through coils that are arranged within a fixed magnetic field. The current generates magnetic fields in the coils and rotate. Brushless motor pump offer high efficiency and simple controllability.

2.1.6 Controller & display. This prototype use ATmega2560 as a microprocessor which has 54 digital input / output, 15 pin as PWM output, 16 analog inputs with 10 bits resolution and 4 UARTs. The LCD 20x4 module was installed as a display and keypad for operating the system.

2.2. System calibration

2.2.1 Temperature sensor. The LM35 sensor are precision integrated-circuit temperature devices with an output voltage linearly-proportional to the temperature. The Horiba water quality checker was used to measure the liquid was entered in the chamber to calibrate the LM35 sensor. A more precise calibration was conducted by making some temperature variations using hot plate. In this case a calibrated water quality checker was used to determine the offset and slope for the linear relation.
2.2.2 Flow sensor. The flow sensor using 5 volt Dc, current 15mA, water discharged range of 0.085 to 5 l/min. Based on the event there is a magnetic field and no magnetic field in the form of square waves. This signal will be calculated to produce a flow rate and the volume that passes through this flow meter. The calibration factor value is calculated based on the pulse generated proportional to the volume in liters passing through the flow meter. The calibration curve justifies in 1 liter of the seawater volume produced a number with pulses constant approximately 340 pulses or 2.9ml / pulse.

2.2.3 pH sensor. Measuring the pH level using the potential difference between a reference and a glass electrode. The small potential difference can be detect using OpAmp at once condition the signal properly to microcontroller. In some case we can use single point calibration and is used to confirm the actual zero point of the pH sensor after we have the slope formula. In order to increase accuracy, it was use standard solution of 4, 6.86, 7, 9 as buffer to calibrate the pH probe. Figure shows the equation calibration was used in the program to calculate pH value.

2.2.4 Conductivity sensor. The conductivity sensor will show the relationship between conductivity and concentration in solution is linear. DS18B20 temperature sensor was pair with the sensor as temperature compensation. This four-point calibration using standard buffer solution of 1413 µs/cm, 4460 µs/cm, 12.88 ms/cm and 36.388 ms/cm was applied. The response of the sensor in the calibration process show in figure 7 and the equation will be used in the program to calculate conductivity value.
2.3 Pre-concentration of cesium using K₄FeCN₆ cartridges filter

2.3.1 Coating filter process. The coating process in 1 micron cotton wounded filter was carried out in two steps by following the reaction mechanism [13]: K₄Fe(CN)₆ + Cu(NO₃)₂ = K₂CuFe(CN)₆ + 2KNO₃. The solution of 10 gram/300ml kalium heksasianoferat (K₄Fe(CN)₆·3H₂O) in deionised water was circulated in the system following the procedure (Buesseler et al.,1990 and Roos et al.,1994). The first step coating process complete after the water turn clear then dried at 80°C for one day. Figure 1 describe the complete preparation steps for coating cotton wounded filter.

![Figure 8. Preparation of hexacyanoferrate cotton wounded filter](image1)

![Figure 9. Preparation of standard filter for calibration](image2)

2.3.2 Standard calibration for filter. The preparation of standard calibration for coated filter follow the procedure of sample but replace the seawater with the pure water. The coated filter that has been ashed at temperature 200°C will be spiked with 1Bq of ¹³⁷Cs standard solution radiotracer. Polypropylene bottle was used as a standard container in homogenized form.

2.4 Laboratory experiments

The experiment in laboratory experiments was conducted to ensure the prototype is capable to use. The prototype was built according to the planned design. All sensors have been calibrated both using calculations based on standard solution and certified devices. Performance testing in the laboratory include comparing measurement results between sensor, standard solution and higher standard devices. On other hand the prototype also tested using the seawater from Jakarta bay for real experiment.

Calculation of filter efficiency. The efficiency collection of radiocesium in the system was calculated from each filter following the formula [10]:

\[ E_{ff} = \frac{(F_2 - F_3)}{F_2} \times 100 \]  

Where \( E_{ff} \) is radiocesium collection efficiency. \( F_2 \) and \( F_3 \) are the activity ¹³⁷Cs in the 2nd and 3rd filter cartridge. The total ¹³⁷Cs activity concentration in the seawater sample calculated following the formula:

\[ A = \frac{F_2}{E_{ff} \times V} \]  

Where \( A \) is the total activity concentration (Bq/l). \( F_2 \) is the activity ¹³⁷Cs in the 2nd cartridge and \( V \) is the volume of seawater through the system (liter).
2.5 Spectrometry measurement

The measurements of $^{137}$Cs were carried out in the gamma spectrometer laboratory, Marine Radioecology – BATAN. The CANBERRA spectrometry instrumentation was used for analysis consists of HPGe detector, multichannel analyzer and high voltage. Standard source $^{152}$Eu was used for energy calibration and standard calibration filter was prepared for efficiency calibration.

3. Implementation and results

The prototype had been successfully created using hardware contains of chamber for sensor, flexible piping and 10 inch cartridge filter housing with NSF Certificate. All part was mounted on light steel that has been coated with anticorrosive paint. This prototype is driven by a microcontroller ATmega 2560 using arduino as minimum system. Laboratory testing was conducted in marine radioecology laboratory - BATAN before the prototype used in the field. The performance characteristics of all mounted sensors except the temperature sensor on the prototype was evaluated using standard solution and calibrated devices. To evaluated the prototype performance of extraction $^{137}$Cs in seawater, was used the standard tracer $^{137}$Cs (6 ± 0.01 Bq/l) spiked in the seawater. This design will replace the old unit without changing the fundamental procedure [12].

3.1 The sensor performance

The first thing that needs to be evaluated in this prototype was performance of the sensor. Comparative measurements were conducted using buffer solution standar and Horiba water quality checker. Figure 10 and 11 informs that the result of sensor measurement capability was comparable. On other hand statistic test also conducted to determine the value of measurement uncertainty.

| Table 1. Statistical test of pH and conductivity sensor |
|---------------------------------|----------------|----------------|----------------|----------------|----------------|
|                                | Ntotal | Mean   | Standard Deviation | Minimum Value | Medium Value | Max Value   |
| pH 7                           | 20     | 7.18   | 0.06               | 7.11           | 7.20          | 7.31        |
| Conductivity                   | 20     | 35.613 | 0.215              | 35.21          | 35.68         | 35.88       |

Figure 10. Measurements of conductivity buffer solution using sensor and Horiba WQC

Figure 11. Measurements of pH buffer solution using sensor and Horiba WQC
Statistical test was taken from 20 times measurements of sample and put the results into statistic software to get the results. The uncertainty measurement provide from statistical test was 7.20 ± 0.06 and 35.68 ± 0.22 or about 1% error respectively. To ensure the reading of the sensor were good, the minimum data to calculate was 10 data.

3.1.1 Static measurements. The measurements were conducted when the solenoid valve was activated by a mounted level sensor in chamber. The flow coming from the entrance to the chamber will be blocked and goes directly to the cartridge filter housing.

![Figure 12. Static measurement performance of pH sensor.](image1)

![Figure 13. Static measurement performance of conductivity sensor.](image2)

Figure 12 and 13 informs the sensor performance measurements in static conditions was very stable. All value of pH and conductivity were never exceeds the upper limit control and lower limit control. Compared to the level of precision, the accuracy of the measuring instrument was more important. If the value changes for conditions in relatively unchanged, then this measurement tool cannot be used.

3.1.2 Dynamic measurements.

![Figure 14. Dynamic measurement performance of pH sensor](image3)

![Figure 15. Dynamic measurement performance of conductivity sensor](image4)
Figure 14 and 15 revealed there were differences in measurement results between static and dynamic measurements. The differences value was 0.20 in pH sensor and 0.24 mS in conductivity sensor. This is due to fluctuations in chamber condition as a result of the flow of fluid through it.

3.2 Determination activity concentration of $^{137}$Cs in seawater.

The main purpose of prototype created was to enhance the effectiveness extraction $^{137}$Cs in seawater and replaced the conventional equipment without fundamental changes to the methods [12]. The important things to consider in determining the activity concentration of $^{137}$Cs in seawater using a filter method was a changing in collection efficiency [14]. Table 1 informs the performance evaluation of the prototype was influence by flow rate. The highest impact of flow rate was pH sensor measurement with changing value up to 0.55 pH. That effect came from the shape of the sensor, the direction of fluid and the mounted location in the chamber.

| Flow rate (l/min) | Temperature (Celsius) | pH    | Conductivity (ms/cm) | Efficiency Extraction | Activity Concentration (Bq/l) |
|-------------------|----------------------|-------|----------------------|-----------------------|--------------------------------|
| 1 l/min           | 29.5                 | 8.05  | 35.58                | 84 %                  | 5.39 Bq/l                      |
| 3 l/min           | 29.7                 | 8.01  | 35.77                | 89 %                  | 5.93 Bq/l                      |
| 5 l/min           | 29.1                 | 7.82  | 35.55                | 87 %                  | 4.39 Bq/l                      |
| 8 l/min           | 29.5                 | 7.85  | 35.61                | 58 %                  | 3.84 Bq/l                      |
| 10 l/min          | 29.8                 | 7.45  | 35.66                | 65 %                  | 2.01 Bq/l                      |

**Table 2. Performance evaluation of the prototype**

Figure 16 and 17 express the effect of flowrate on the activity concentration and efficiency collection of $^{137}$Cs in seawater. The optimum flowrate to achieve a good results was 3l/min. Although the slower flowrate make a longer time to contact between $^{137}$Cs and ion exchanger [13]. However the possibility the flow unable to penetrate deeper into the filter pores. To resolve this problem we set the flow rate from the pump in 3l/min for all the time.
4. Conclusion
The prototype of seawater sampling has been successfully made and met the quality control chart in measurement water quality parameter. Overall quality of sensor performance both static and dynamic measurements was still in range of control chart. However based on the design of prototype it strongly recommended using static measurements mode for the best result. The pumping flow rate is greatly affect in determination of 

\[ ^{137}\text{Cs} \] and the best flowrate are 3l/min. This unit fulfilled quality control chart in water quality checker measurement. According to IAEA analytical guidelines the results of decision threshold and detection limit were 0.13 mBq/l and 0.29 mBq/l respectively, also the results of the relative bias and precision test are below the permissible limit. This prototype also capable to replace the previous equipment to achieve higher collection efficiency of 

\[ ^{137}\text{Cs} \] and very easy to relocated

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